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# PRELIMINARY INVESTIGATION OF EFFECTS ON THE ENVIRONMENT OF BORON, INDIUM NICKEL, SELENIUM, TIN, VANADIUM AND THEIR COMPOUNDS

## VOLUME I - BORON

VERSAR, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

AUGUST 1975

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# PRELIMINARY INVESTIGATION OF EFFECTS ON THE ENVIRONMENT OF BORON, INDIUM NICKEL, SELENIUM, TIN, VANADIUM AND THEIR COMPOUNDS

## VOLUME I

## BORON

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# PRELIMINARY INVESTIGATION OF EFFECTS ON THE ENVIRONMENT OF BORON, INDIUM NICKEL, SELENIUM, TIN, VANADIUM AND THEIR COMPOUNDS

Volume I

Boron

Contract No. 68-01-2215

Project Officer

Farley Fisher

Prepared for

Office of Toxic Substances
Environmental Protection Agency
Washington, D.C. 20460

August 1975

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BORON

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Volume I

# Preliminary Investigation of Effects on Environment of Boron and Its Compounds

## FOREWORD

This is Volume I of a series of six reports on the environmental effects of boron, indium, nickel, selenium, tin, and vanadium and their compounds. The information is based on literature reviews, direct contact with representatives of companies involved in the production or use of the materials, and consultation with knowledgeable individuals from industry, academic institutions and the Federal Government.

.. BORON INDUSTRY IN THE UNITED STATES

A. Producers and Sites

Table 1 lists commercially significant chemical products and the companies involved. For this study significant is defined as production exceeding 1/2 metric ton or $1,000 value. Other materials may also be included in the discussion because of their unusual properties, such as toxicity, or their anticipated future significance.

Table 1

Boron Products and Producers[1]

| Chemical | Producer: Company, subordination | Location |
|---|---|---|
| Aluminum diboride | Alfa Products Div. | Beverly, Mass. |
| Ammonium borate (Ammonium acid tetraborate) | U.S. Borax & Chem. Corp. | Wilmington, Del. |
| Ammonium fluoborate (Ammonium borofluoride) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Kawecki Berylco Indust., Inc. | Boyertown, Pa. |
| | Kewanee Oil Co., Harshaw Chem. Co., Indust. Chems. Dept. | Cleveland, Ohio |
| Antimony fluoborate | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Norton Chem. Corp. | Brooklyn, N.Y. |
| Barium borofluorostannate | City Chem. Corp. | Jersey City, N.J. |
| Boric acid (Boracic acid) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Kerr-McGee Corp. Kerr-McGee Chem. Corp., subsid. | Trona, Calif. |
| | Stauffer Chem. Co. Indust. Chem. Div. | San Francisco, Calif. |
| | U.S. Borax & Chem. Corp. | Wilmington, Calif. |
| Boric acid esters | U.S. Borax & Chem. Corp. | Boron, Calif. |
| Borax | Belmont Smelting & Refining Works, Inc. | Brooklyn, N.Y. |
| | Fairmount Chem. Co., Inc. | Newark, N.J. |
| | Kawecki Berylco Indust., Inc. | Boyertown, Pa. |

Table 1 (Con't)
Boron Products and Producers (1)

| Chemical | Producer<br>Company, subordination | Location |
|---|---|---|
| Boron (Con't) | Kerr-McGee Corp.<br>Kerr-McGee Chem. Corp., subsid. | Henderson, Nev. |
| | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp., subsid. | Anaheim, Calif. |
| | Ventron Corp.<br>Chems. Div. | Wood Ridge, N.J. |
| Boron carbide | Apache Chems., Inc. | Rockford, Ill. |
| | Fairmount Chem. Co., Inc. | Newark, N.J. |
| | Kawecki Beryloo Indust., Inc. | Boyertown, Pa. |
| | Norton Co. | Worcester, Mass. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Boron fluoride-ethylamine complex (Ethylamine boron trifluoride) | Kawanee Oil Co.<br>Harshaw Chem. Co., div.<br>Indust. Chems. Dept. | Cleveland, Ohio |
| | Ozark-Mahoning Co. | Tulsa, Okla. |
| Boron fluoride orthophosphoric acid | Kawanee Oil Co.<br>Harshaw Chem. Co., div.<br>Indust. Chems. Dept. | Cleveland, Ohio |
| Boron nitride | The Carborundum Co.<br>Refractories and Electronics Div. | Latrobe, Pa. |
| | Fairmount Chem. Co., Inc. | Newark, N.J. |
| | Kawecki Beryloo Indust., Inc. | Boyertown, Pa. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Boron oxide | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Eagle-Picher Indust., Inc.<br>Electronics Div. | Miami, Okla.<br>Quapaw, Okla. |
| | Stauffer Chem. Co.<br>Indust. Chem. Div. | San Francisco, Calif. |
| Boron phosphate | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Boron phosphide | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |

Table 1 (Con't)
Boron Products and Producers (1)

| Chemical | Producer<br>Company, subordination | Location |
|---|---|---|
| Boron tribromide | Eagle-Picher Indust., Inc.<br>Electronics Div. | Miami, Okla.<br>Quapaw, Okla. |
| | Kerr-McGee Corp.<br>Kerr-McGee Chem. Corp., subsid. | Henderson, Nev. |
| Boron trichloride | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Kerr-McGee Corp.<br>Kerr-McGee Chem. Corp., subsid. | Henderson, Nev. |
| Boron trifluoride | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Kewanee Oil Co.<br>Harshaw Chem. Co., div.<br>Indust. Chems. Dept. | Cleveland, Ohio<br>Cleveland, Ohio |
| Boron trifluoride ethyl ether complex | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| Boron trifluoride-phenol complex | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| Boron triiodide | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Boroxines (unspecified) | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| Calcium borate | Tennco Inc.<br>Tennco Oil Co., Div. | Death Valley Junction, Calif. |
| | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp., subsid. | Anaheim, Calif. |
| Calcium boride (calcium hexaboride) | Molybdenum Corp. of America<br>Chems. and Rare Earth Div. | Washington, Pa. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Chromium boride (mono) | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp. | Anaheim, Calif. |
| | Ventron Corp., Alfa Products Div. | Beverly, Mass. |
| Chromium fluoborate | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| Cobalt borate (Cobaltous borate) | The Shepherd Chem. Co. | Cincinnati, Ohio |
| Cobalt fluoborate (Cobaltous fluoborate) | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | Ventron Chem. Corp.<br>Alfa Products Div. | Beverly, Mass. |

Table 1 (Con't)
Boron Products and Producers (1)

| Chemical | Producer: Company, subordination | Location |
|---|---|---|
| Copper borate (Cupric borate) | City Chem. Corp. | Jersey City, N.J. |
| | The Shepherd Chem. Co. | Cincinnati, Ohio |
| Copper fluoborate (Cupric fluoborate) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | Kewanee Oil Co. Harshaw Chem. Co. Indust. Chems. Dept. | Cleveland, Ohio |
| Indium fluoborate | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | The Indium Corp. of America | Utica, N.Y. |
| Iron borate (Ferric borate) | City Chem. Corp. | Jersey City, N.J. |
| Iron fluoborate (Ferrous fluoborate) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| Lead borate | Humphrey Chem. Corp. | Edgewood Arsenal, Md. |
| | The Shepherd Chem. Co. | Cincinnati, Ohio |
| Lead fluoborate (Plumbous fluoborate) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | Kewanee Chem. Co. Harshaw Chem. Co. Indust. Chems. Dept. | Cleveland, Ohio |
| Lithium borohydride | Mine Safety Appliances Co. Callery Chem. Co. | Callery, Pa. |
| | Ventron Corp. Alfa Products Div. Chems. Div. | Beverly, Mass. |
| Lithium fluoroborate | Foote Mineral Co. | Exton, Pa. |
| | Ozark-Mahoning Co. | Tulsa, Okla. |
| | Ventron Corp. Alfa Products Div. | Beverly, Mass. |
| Magnesium borate | The Shepherd Chem. Co. | Cincinnati, Ohio |
| Magnesium fluoborate | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Kewanee Oil Co. Harshaw Chem. Co. Indust. Chems. Dept. | Cleveland, Ohio |

Table 1 (Con't)
Boron Products and Producers (1)



| Chemical | Producer<br>Company, subordination | Location |
|---|---|---|
| Manganese borate<br>(Manganous borate) | Chemetron Corp., Chems.<br>Group, Inorganic Chems. Div. | Cleveland, Ohio |
| | Gen. Metallic Oxides Co. | Jersey City, N.J. |
| | The Shepherd Chem. Co. | Cincinnati, Ohio |
| Manganese boride | Molybdenum Corp. of America<br>Chems. and Rare Earth Div. | Washington, Pa. |
| Manganese fluoborate<br>(Manganous fluoborate) | City Chem. Corp. | Jersey City, N.J. |
| Molybdenum boride, mono<br>, di- | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp. | Anaheim, Calif. |
| Nickel fluoborate<br>(Nickelous fluoborate) | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | American Cyn Co.<br>M&T Chems., Inc. | East Chicago, Ind. |
| | Burstan Chem. Corp. | Brooklyn, N.Y. |
| | Kewanee Oil Co.<br>Harshaw Chem. Co.<br>Indust. Chems. Dept. | Cleveland, Ohio |
| | Ozark-Mahoning Co. | Tulsa, Okla. |
| | Ventron Corp., Alfa<br>Products Div. | Beverly, Mass. |
| Niobium boride<br>(Niobium diboride) | Kawecki Beryloo Indust., Inc. | Boyertown, Pa. |
| | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp. | Anaheim, Calif. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Phosphine borane | Mine Safety Appliances Co.<br>Callery Chem. Co. | Callery, Pa. |
| Potassium borohydride | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | Ventron Corp.<br>Chems. Div. | Beverly, Mass. |
| Potassium fluoborate | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Borden Inc.<br>Borden Chem. Div.<br>Smith-Douglass | Plant City, Fla. |
| | Kawecki Beryloo Indust., Inc. | Boyertown, Pa. |
| | Kewanee Oil Co.<br>Harshaw Chem. Co. div.<br>Indust. Chems. Dept. | Cleveland, Ohio |

Table 1 (Con't)
Boron Products and Producers (1)



| Chemical | Producer: Company, subordination | Location |
|---|---|---|
| Potassium fluoborate (con't) | Ozark-Mahoning Co. | Tulsa, Okla. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Rubidium borohydride | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Silicon hexaboride (Hexaboron silicide) | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Silicon tetraboride | Mallinckrodt Chem. Works<br>Indust. Chems. Div. | St. Louis, Mo. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Silver fluorborate | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | Ozark-Mahoning Co. | Tulsa, Okla. |
| | Ventron Corp.<br>Alfa Chems. Div. | Beverly, Mass. |
| Sodium borodeuteride | Ventron Corp.<br>Alfa Products Div.,<br>Chems. Div. | Beverly, Mass.<br>Beverly, Mass. |
| Sodium borohydride | Mine Safety Appliances, Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | Ventron Corp.<br>Alfa Products Div.<br>Chems. Div. | Beverly, Mass.<br>Beverly, Mass. |
| Sodium fluoborate (Sodium borofluoride) | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Kawecki Beryleo Indust., Inc. | Boyertown, Pa. |
| | Kawanee Oil Co.<br>Harshaw Chem. Co., div.<br>Indust. Chems. Dept. | Cleveland, Ohio |
| | Ozark-Mahoning Co. | Tulsa, Okla. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Sodium metaborate | U.S. Borax & Chem. Corp. | Wilmington, Calif. |
| Sodium pentaborate | Kerr-McGee Corp.<br>Kerr-McGee Chem. Corp., subsid. | Crosby, Texas |
| Sodium perborate, monohydrate | FMC Corp.<br>Inorganic Chems. Div. | Buffalo, N.Y. |

Table I (Con't)

Boron Products and Producers[1]

| Chemical | Producer: Company, subordination | Location |
|---|---|---|
| Sodium perborate tetrahydrate (Sodium metaborate peroxyhydrate) | E. I. duPont de Nemours & Co., Inc. Indust. Chems. Dept. | Memphis, Tenn. |
| | Filo Color & Chem. Corp. | Newark, N.J. |
| | FMC Corp. Inorganic Chems. Div. | Buffalo, N.Y. |
| Sodium tetraborate (Borax) (Produced as Anhydrous Borax, Borax decahydrate, and Borax pentahydrate) | Kerr-McGee Corp. Kerr-McGee Chem. Corp., subsid. | Trona, Calif. |
| | Occidental Petroleum Corp. Searles Lake Chem. Co., subsid.* | Searles Lake, Calif. |
| | Stauffer Chem. Co. Indust. Chem. Div. | West End, Calif. |
| | U.S. Borax & Chem. Corp. | Boron, Calif. |
| Sodium tetraphenylboron (Sodium tetraphenylborate) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Richardson-Merrell, Inc. J.T. Baker Chem. Co., subsid. | Phillipsburg, N.J. |
| Tantalum diboride | Kawecki Beryloo Indust., Inc. | Boyertown, Pa. |
| Tin fluoborate (Stannous fluoborate) | Allied Chem. Corp. Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | Kewanee Chem. Corp. Harshaw Chem. Co. Indust. Chems. Dept. | Cleveland, Ohio |
| Titanium diboride (Titanium boride) | Kawecki Beryloo Indust., Inc. | Boyertown, Pa. |
| | U.S. Borax & Chem. Corp. U.S. Borax Research Corp. | Anaheim, Calif. |
| | Ventron Corp. Alfa Products Div. | Beverly, Mass. |
| Tungsten monoboride | U.S. Borax & Chem. Corp. U.S. Borax Research Corp. | Anaheim, Calif. |
| Vanadium diboride | U.S. Borax & Chem. Corp. U.S. Borax Research Corp. | Anaheim, Calif. |
| | Ventron Corp., Alfa Products Div. | Beverly, Mass. |
| Zinc borate | Humphrey Chem. Corp. | Oakwood Annex, Mi. |
| | Maryland Zinc & Research Co. | Cockeysville, Md. |
| | U.S. Borax & Chem. Corp. | Wilmington, Calif. |
| | Ventron Corp. Alfa Products Div. | Beverly, Mass. |

Table 1 (Con't)
Boron Products and Producers (1)

| Chemical | Producer<br>Company, subordination | Location |
|---|---|---|
| Zinc fluoborate | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Harstan Chem. Corp. | Brooklyn, N.Y. |
| | Kewanee Oil Co.<br>Harshaw Chem. Co.<br>Indust. Chems. Dept. | Cleveland, Ohio |
| | Mineral Research and Dev. Corp. | Concord, N.C. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Zirconium diboride (Zirconium boride) | Kawecki Beryloo Indust. Inc. | Boyertown, Pa. |
| | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp. | Anaheim, Calif. |
| | **BORANES (Inorganic)** | |
| Decaborane | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| Diborane | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | G. D. Searle & Co.<br>Will Ross, Inc., subsid.<br>Matheson Gas Products, div. | Cucamonga, Calif.<br>East Rutherford, N.J.<br>Gloucester, Mass.<br>Joliet, Ill.<br>La Porte, Tex.<br>Morrow, Ga.<br>Newark, Calif. |
| Octadecaborane | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Pentaborane | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | **ORGANIC BORON COMPOUNDS** | |
| Dimethylamine borane | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| Dioxaborinanes | U.S. Borax & Chem. Corp. | Anaheim, Calif. |

Table I (Con't)
Boron Products and Producers (1)

| Chemical | Producer: Company, subordination | Location |
|---|---|---|
| Hexylene borate | Kipers Labs. | Santa Ana, Calif. |
| Morpholine borane | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| | Chems. Div. | Beverly, Mass. |
| Sodium tetraphenylboron (Sodium tetraphenylborate) | Allied Chem. Corp.<br>Specialty Chems. Div. | Marcus Hook, Pa. |
| | Richardson-Merrell, Inc.<br>J.T. Baker Chem. Co., subsid. | Phillipsburg, N.J. |
| tert-Butylamine borane | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Trialkyl boranes | Stauffer Chem. Co.<br>Specialty Chem. Div. | Weston, Mich. |
| Tributyl borate (Butyl borate) | Anderson Dev. Co. | Adrian, Mich. |
| Tri-m, p-cresyl borate | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp., subsid. | Anaheim, Calif. |
| Tricyclohexyl borate | Anderson Dev. Co. | Adrian, Mich. |
| Triethanolamine borate | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp., subsid. | Anaheim, Calif. |
| Triethylborane (Triethylboron) | Mine Safety Appliances Co.<br>Callery Chem. Co., div. | Callery, Pa. |
| | Texas Alkyls, Inc. | Deer Park, Tex. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Triethyl borate (Triethoxy borane) | Anderson Dev. Co. | Adrian, Mich. |
| | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp., subsid. | Anaheim, Calif. |
| Triethyloxonium tetrafluoroborate | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |
| Tri (hexylene glycol) biborate | U.S. Borax & Chem. Corp.<br>U.S. Borax Research Corp., subsid. | Anaheim, Calif. |
| Triisobutylborane | Texas Alkyls, Inc. | Deer Park, Tex. |
| Triisopropyl borate | Anderson Dev. Co. | Adrian, Mich. |
| | Stauffer Chem. Co.<br>Specialty Chem. Div. | Weston, Mich. |
| | Ventron Corp.<br>Alfa Products Div. | Beverly, Mass. |

Table 1 (Cont)
Boron Products and Producers (1)

| Chemical | Producer: Company, subordination | Location |
|---|---|---|
| Trimethoxyboroxine (Methyl metaborate) | Mine Safety Appliances Co. Callery Chem. Co., div. | Callery, Pa. |
| | Stauffer Chem. Co. Specialty Chem. Div. | Weston, Mich. |
| Tri-2-methoxyethyl borate | Anderson Dev. Co. | Adrian, Mich. |
| Trimethyl borate (Methyl borate) (Trimethoxyborine) | Anderson Dev. Co. | Adrian, Mich. |
| | Mine Safety Appliances Co. Callery Chem. Co., div. | Callery, Pa. |
| | Stauffer Chem. Co. Specialty Chem. Div. | Weston, Mich. |
| | Ventron Corp. Chem. Div. | Danvers, Mass. |
| Trimethyl borate-methanol azeotrope | Ventron Corp. Alta Products Div. | Beverly, Mass. |

* Scheduled late 1974

B. Costs and Physical Properties of Important Boron Compounds

The prices of selected boron minerals and chemicals are given in Table 2. The materials listed are the most commercially significant of the boron family. Another common factor is that their most important applications are based on their boron oxide ($B_2O_3$) content. In many instances these materials are interchangeable. In 1970 anhydrous borax was the least expensive in $B_2O_3$ content, but under 1974 prices borax pentahydrate is cheapest. Physical properties of the most important boron compounds are presented in Table 3.

Many metals form borides of various compositions. Most are specialty materials only, but a few are used in the aerospace industry. In general, environmental effects are minimal.

Many of the metal borides oxidize in air considerably below the listed melting points. This limits the significance of the high melting points (e.g., vanadium and tungsten borides oxidize in air at less than 1200C versus listed melting points of 2000 - 3000C. As a rule the melting point of a particular boride composition increases with the atomic weight in a Group but decreases with increasing atomic weight in each period. Hafnium and tantalum borides therefore have the highest melting points - 3250 ± 100C and 3400 ± 50C.

Table 3
(2)
Prices of Boron Minerals and Chemicals

| | | $B_2O_3$ Content, % | Price in Carlots, f.o.b. Plant | | | |
|---|---|---|---|---|---|---|
| | | | 1970 Prices ($) | | 1974 Prices ($) | |
| | | | per metric ton | per unit $B_2O_3$ | per metric ton | per unit $B_2O_3$ |
| Borax decahydrate | bags | 36.3 | 53 | 1.47 | 73 | 2.01 |
| | bulk | 36.3 | 45 | 1.24 | 60 | 1.65 |
| Borax pentahydrate | bags | 47.56 | 68 | 1.43 | 86 | 1.81 |
| | bulk | 47.56 | 60 | 1.26 | 73 | 1.53 |
| Anhydrous borax | bags | 68.5 | 93 | 1.36 | 159 | 2.33 |
| | bulk | 68.5 | 84 | 1.26 | 145 | 2.12 |
| Boric acid | bags | 56.44 | 113 | 2.01 | 169 | 3.01 |
| | bulk | 56.44 | 104 | 1.83 | 148 | 2.63 |
| Boric oxide | bags | 99.3 | 360 | 3.62 | 573 | 57.2 |
| | bags | 95-96 | 159 | 1.67 | | |
| | bulk | 95-96 | 149 | 1.56 | | |

Table 3

Physical Properties

| Chemical | Specific Gravity | Melting Point °C | Boiling Point °C | Solubility Water g/100cc °C | Comments |
|---|---|---|---|---|---|
| Boron | 2.34 crys<br>2.37 amor | 2300 | 2550 sub | Insol. | 0.001% earth's crust<br>combined form only |
| Sodium tetraborate Decahydrate (Borax) | 1.73 | 75 | 320<br>$-10H_2O$ | 2.01 @ 0<br>170 @ 100 | Natural mineral<br>% $B_2O_3$ - 36.3 |
| Sodium tetraborate Pentahydrate | 1.815 | 120<br>$-H_2O$ | --<br>1575 | 22.65 @ 65<br>52.3 @ 100 | Natural mineral<br>% $B_2O_3$- 47.5 |
| Sodium tetraborate Anhydrous | 2.67 | 741 | d | 1.05 @ 0<br>8.79 @ 40 | % $B_2O_3$- 68.5 |
| Colemanite* | 2.42-<br>2.43 | -- | -- | -- | Natural mineral |
| Boric Acid | 1.435<br>15°C | 169<br>to $HBO_2$ | 300<br>$-1\ 1/2\ H_2O$ | $6.35^{30}$<br>$27.6^{100}$ | $H_3BO_3$<br>Ortho form |
| Boric oxide | 2.46 crys<br>1.812 glass | 460 | 1860 | $1.1$<br>$15.7^{100}$ | boron trioxide |
| Boron trifluoride | 2.99 g/l (gas) | -126.7 | -99.9 | 106 cold<br>d hot | fumes in moist air<br>pungent odor |
| Boron trichloride | $1.349_4^{11}$** | -107.3 | 12.5 | d hot | fumes in moist air<br>emits hydrogen chloride |
| Sodium fluoborate | $2.47^{20}$ | sl d<br>384 | d | $108^{26}$<br>$210^{100}$ | |
| Potassium fluoborate | $2.498^{20}$ | d350 | d | $0.44^{20}$<br>$6.27^{100}$ | Natural<br>avogadrite |
| Ammonium fluoborate | $1.871^{15}$ | subl | -- | $25^{16}$<br>$97^{100}$ | |

*$Ca_2B_{12}O_{11} \cdot 5H_2O$

**g.sp. at 11°C referenced to water at 4°C

Table 3 (Cont'd)

Physical Properties

| Chemical | Specific Gravity | Melting Point °C | Boiling Point °C | Solubility in Water g/100cc °C | Comments |
|---|---|---|---|---|---|
| Diborane | Liq. 0.447 -11 | -165.5 | -92.5 | sl. s., 3 cold water | Boron hydride |
| boron (tetra) carbide | 2.52 | 2370 | 73500 | i | |
| Boron nitride | 2.25 | subl ca 3000 | -- | i cold, sl d hot | |

II. PRODUCTION

A. Natural Sources of Borates

The map in Figure 1[3] shows the location of the significant borate deposits in the United States. They produce virtually all of the raw materials for the boron industry in the U.S. Approximately 20% of the present production stems from the utilization of Searles Lake brines. Significant colemanite (Table 3) mining is also performed by Tenneco. Total borate production by company and location is presented in Table 4.

B. Manufacturing Processes

1. Elemental Boron

Although widespread in nature boron occurs naturally only in combined form. Elemental boron is not one of the more important commercial forms of boron.

Three general techniques are used to prepare boron from its compounds: (1) Chemical reduction with active elements, (2) Non-aqueous electrolytic reduction, and (3) Thermal decomposition. Reduction of boron compounds to elemental boron has been carried out with magnesium, hydrogen, and many other elements. Among the boron compounds used are borates, boron oxides, boron halides, fluoborates, and borohydrides. The most common method for producing large amounts of elemental boron is the exothermic reduction (thermit reaction) of boric oxide with magnesium. The product of this reaction, a finely-divided powder known as "Moissan's boron" is amorphous as is boron produced from any of the chemical reduction methods except for high temperature reduction by hydrogen. The latter method, especially when involving hot filament reaction of hydrogen with boron tribromide, has become a conventional means for obtaining boron with purities of 99% and higher.

Electrolytic preparation of boron usually involves the passage of a current through fused melts of boric oxide in potassium halides or oxides. Electrolysis of potassium fluoborate-potassium chloride or potassium chloride-sodium chloride melts is performed with a boron carbide anode. The purity of the product obtained by these methods has been 87-99.8%. Direct electrolysis

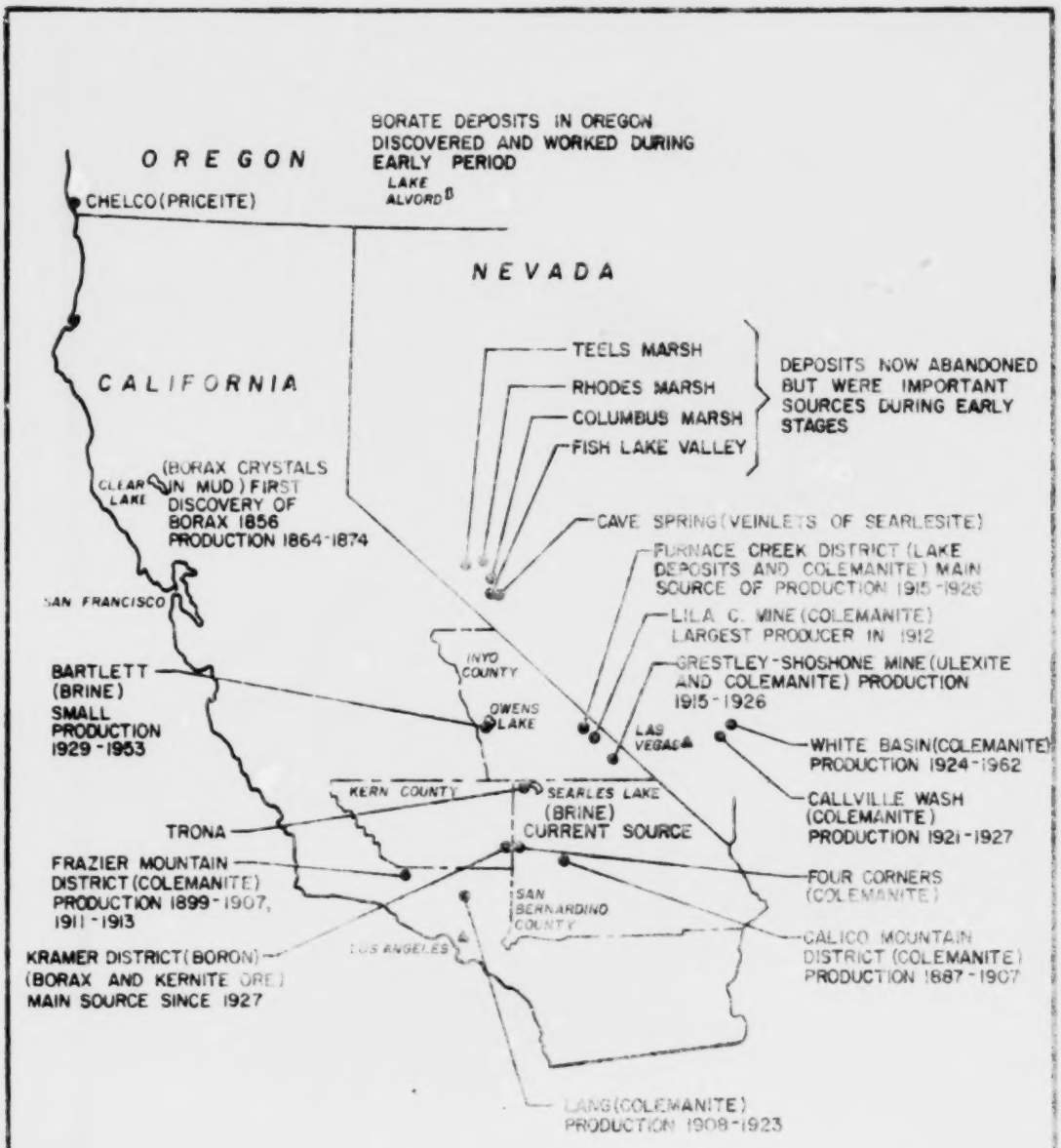
BORATE DEPOSITS IN OREGON DISCOVERED AND WORKED DURING EARLY PERIOD
OREGON
LAKE ALVORD
CHELCO (PRICEITE)
NEVADA
CALIFORNIA
TEELS MARSH
RHODES MARSH
COLUMBUS MARSH
FISH LAKE VALLEY
DEPOSITS NOW ABANDONED BUT WERE IMPORTANT SOURCES DURING EARLY STAGES
CLEAR LAKE
(BORAX CRYSTALS IN MUD) FIRST DISCOVERY OF BORAX 1856 PRODUCTION 1864-1874
CAVE SPRING (VEINLETS OF SEARLESITE)
FURNACE CREEK DISTRICT (LAKE DEPOSITS AND COLEMANITE) MAIN SOURCE OF PRODUCTION 1915-1926
SAN FRANCISCO
LILA C. MINE (COLEMANITE) LARGEST PRODUCER IN 1912
INYO COUNTY
BARTLETT (BRINE) SMALL PRODUCTION 1929-1953
OWENS LAKE
GRESTLEY-SHOSHONE MINE (ULEXITE AND COLEMANITE) PRODUCTION 1915-1926
LAS VEGAS
WHITE BASIN (COLEMANITE) PRODUCTION 1924-1962
KERN COUNTY
SEARLES LAKE (BRINE) CURRENT SOURCE
CALLVILLE WASH (COLEMANITE) PRODUCTION 1921-1927
TRONA
FRAZIER MOUNTAIN DISTRICT (COLEMANITE) PRODUCTION 1899-1907, 1911-1913
FOUR CORNERS (COLEMANITE)
SAN BERNARDINO COUNTY
LOS ANGELES
CALICO MOUNTAIN DISTRICT (COLEMANITE) PRODUCTION 1887-1907
KRAMER DISTRICT (BORON) (BORAX AND KERNITE ORE) MAIN SOURCE SINCE 1927
LANG (COLEMANITE) PRODUCTION 1908-1923

Figure 1

Location of Borate deposits

in California, Nevada and Oregon

Table 4
(4)
Production of Borates in the United States
as of 1972

| Company | Quantity | Location | Products |
|---|---|---|---|
| U.S. Borax & Chemical Corp. | 500,000 metric tons as $B_2O_3$ combined annual capacity | Boron, California | crude borax<br>refined borax<br>anhydrous borax<br>boric acid<br>boric oxide |
| Kerr-McGee Chemical Corp. | approx. 100,000 metric tons $B_2O_3$ capacity | Searles Lake, Trona, California | boron compounds |
| Stauffer Chem. Corp. | 25-30,000 metric tons $B_2O_3$ capacity | Searles Lake, Trona, California | boron compounds |
| Tenneco Oil Company | Design-150,000 metric tons raw colemanite<br>Design- 70,000 metric tons calcined colemanite<br>Production: metric tons calcined colemanite 6,300 metric tons | Furnace Creek, California | colemanite ore<br>calcined colemanite |
| Searles Lake Chem. Co. Subsid. of Occidental Pet. Corp. | 24,000 metric tons* | Searles Lake, Calif. | borax |

*Scheduled late 1974. May be indefinitely postponed.

of alkali or alkaline earth borates yields a product of lower purity. Electrolysis has not been an important commercial method for the production of elemental boron.

Boron compounds that can be decomposed to high purity forms of boron are limited to the halides and hydrides. Boron tribromide, boron triiodide, and boron hydrides (from diborane to decaborane) have been decomposed on a wide variety of substrates ranging from glass to tungsten at temperatures from 800 to 1500C.[5]

2. Borax

The entire U.S. production of borax is carried out in the desert areas of California by two processes. The borax ore is either mined and extracted or, as in Searles Lake, taken from the brines by the Trona process.

a. The Mining Process

The mining operation starts at the larger, deep open pit mines. Explosives and electric shovels break up the ore. An automatic ore conveyor belt, starting in the pit at the 225 foot level, then carries the ore to the surface and nearby concentrating and refining plants. This natural material is principally borax (sodium tetraborate decahydrate) and kernite (sodium tetraborate tetrahydrate). Both of these minerals must be processed to remove impurities and produce the primary commercial compounds:

(1) sodium tetraborate decahydrate;
(2) sodium tetraborate pentahydrate; and
(3) anhydrous sodium tetraborate.

The refining process begins by crushing and dissolving the ore to remove the impurities. The ore is next thickened, recrystallized and dried. Some of the material is crystallized and produced as decahydrate, some as pentahydrate. The remainder is fused in a furnace to the anhydrous state. (Figure 2) Wastewater treatment consists of percolation-proof evaporation ponds. The [illegible] plant effluent and the intake water and wastewater sent to the evaporation ponds are thoroughly monitored.[3,6]

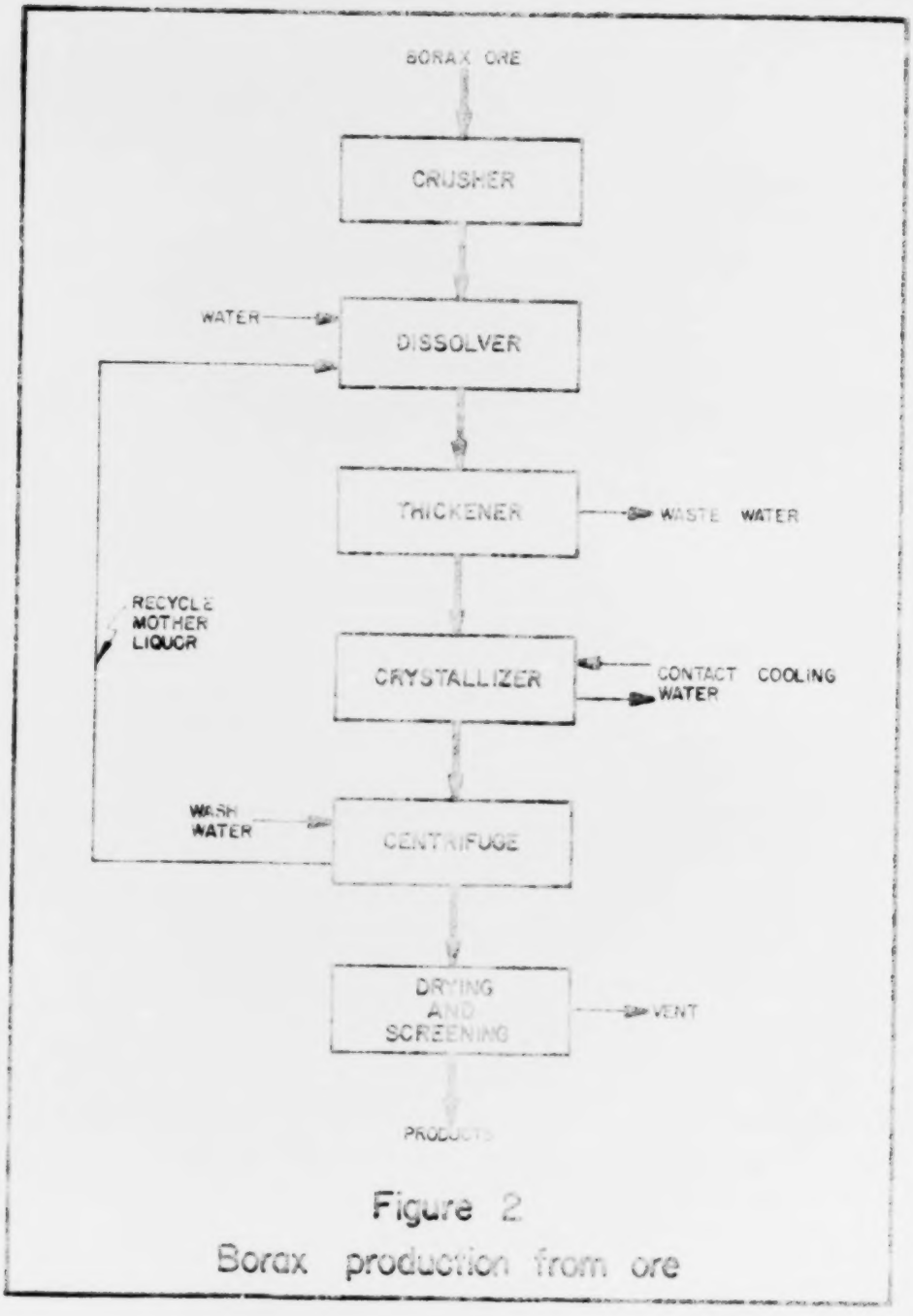


Figure 2

Borax production from ore

b. Trona Process

Brine from Searles Lake is processed to produce borax and other chemicals at two highly integrated facilities located at Trona, California. The recovery processes and raw materials are unique to this location. The area is desert land immediately adjacent to Searles Lake, a large residual evaporate salt body filled with saline brines. The brines are pumped into the processing facilities. The procedures used to yield crude borax are shown in Figure 3. The residual brines, salts, end liquors, and added process waters are returned to the salt body to maintain the saline brine volume. The recycle liquors are actually the medium for producing the raw material for the processes so there is not a "discharge". The crude borax combined with borax solids from the separate carbonation-refrigeration process, is purified by recrystallization, dried, and packaged.(3)

3. Anhydrous Borax

Anhydrous borax is either made from coarse granular decahydrate or from wet decahydrate from the centrifuges. Figure 4 shows a diagram of one process used for the manufacture of anhydrous borax. Two features of this process deserve comment. First, the dust from the calciners is recovered and reprocessed and second, the product can be obtained in either the crystalline or amorphous form. Commercial anhydrous borax is mainly the latter type.(7)

4. Boric Acid

Boric acid is made by reacting borax and sulfuric acid. Since the U.S. sources of borax production are in the California desert areas, that is where the boric acid production is located. Approximately 70 percent of U.S. production of boric acid is based on borax from mined ore, the remainder comes from borax extracted from lake brines.

To produce boric acid from the mined ore borax tetraborate and sulfuric acid are reacted and the resulting slurry is vacuum filtered. The solid boric acid is dissolved in water, filtered, recrystallized, dried, separated by centrifugation, washed, dried, and packaged. The mother liquor is recycled with excess liquor wasted because of water imbalance. Diagram of

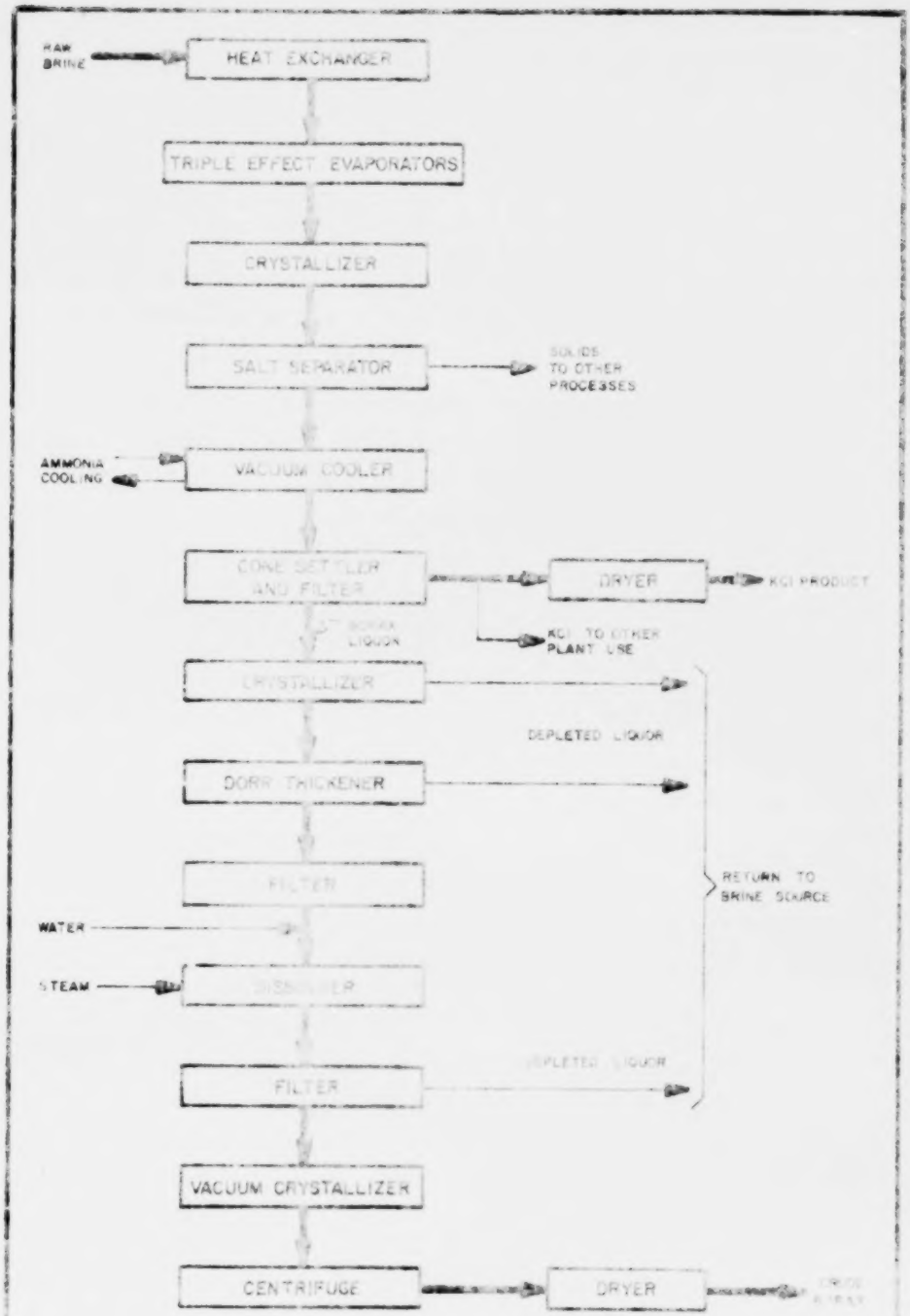


Figure 3

Borax manufacture from Searles Lake brine

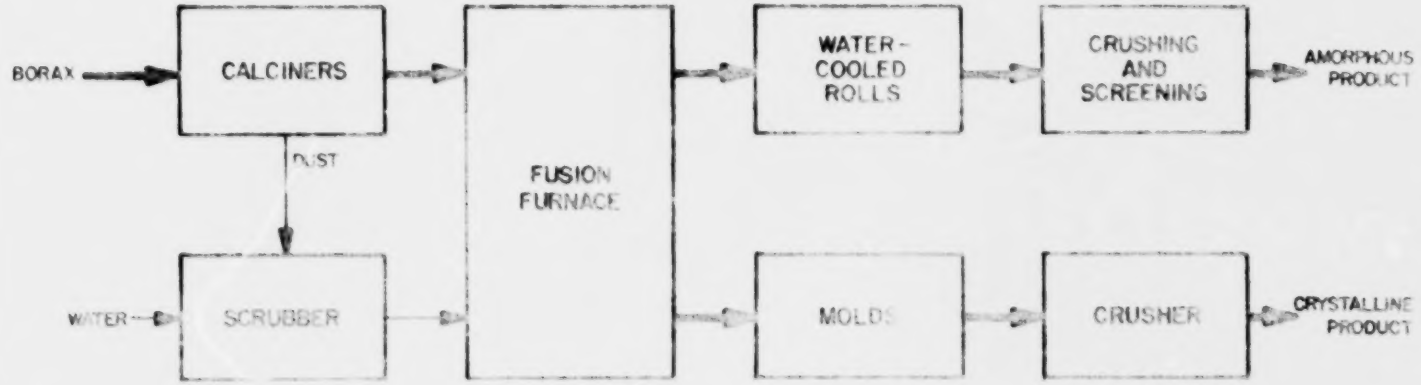


Figure 4

Anhydrous Borax process

processes used at two installations are shown in Figures 5 and 6.[3]

5. Boric oxide ($B_2O_3$, boron trioxide)

Boric oxide may be prepared by the fusion of boric acid. If this method is used, the boric oxide generally contains up to 0.5% water, depending on the temperature and other fusion parameters. If the temperature is at least 1300C, the product is nearly anhydrous. If ground boric acid is heated slowly to 260-270C in a 1 to 2 mm mercury vacuum and maintained at this temperature for six hours, an active, practically anhydrous form of boric oxide is produced. This boric oxide dissolves very rapidly in water with a hissing sound.[5]

6. Boron trifluoride ($BF_3$)

Two processes are in general commercial use for the production of boron trifluoride. In one, borax is added slowly to hydrofluoric acid to produce water and $Na_2O(BF_3)_4$. The latter, "fluoborax", is treated with cold fuming sulfuric acid in a generator. The reaction mixture is slowly heated. The generation of boron trifluoride is controlled by the temperature. This method can also be used by mixing boric acid with ammonium bifluoride, in which case the boron trifluoride complex from which boron trifluoride is generated is $(NH_4)_2O(BF_3)_4$. The other commercial process is to react fluorosulfonic acid with boric acid.[8]

7. Boron trichloride

Boron trichloride is commercially produced by several different methods. One method is by chlorinating a mixture of finely divided carbon and boric oxide at 870 to 980 C. A second method is heating boric oxide with sodium, potassium, or lithium chloride at 800 to 1000C. Between 500 and 1500C sodium borofluoride and magnesium chloride can also be combined to produce boron trichloride.[8]

8. Diborane and higher boranes (pentaborane, etc.)

Diborane is prepared by the reaction of boron trichloride with lithium aluminum hydride in anhydrous diethyl ether or with lithium hydride, sodium borohydride, or sodium trimethoxyborohydride in diethyl ether solution. The higher boranes are produced by the controlled pyrolysis of diborane.[8]

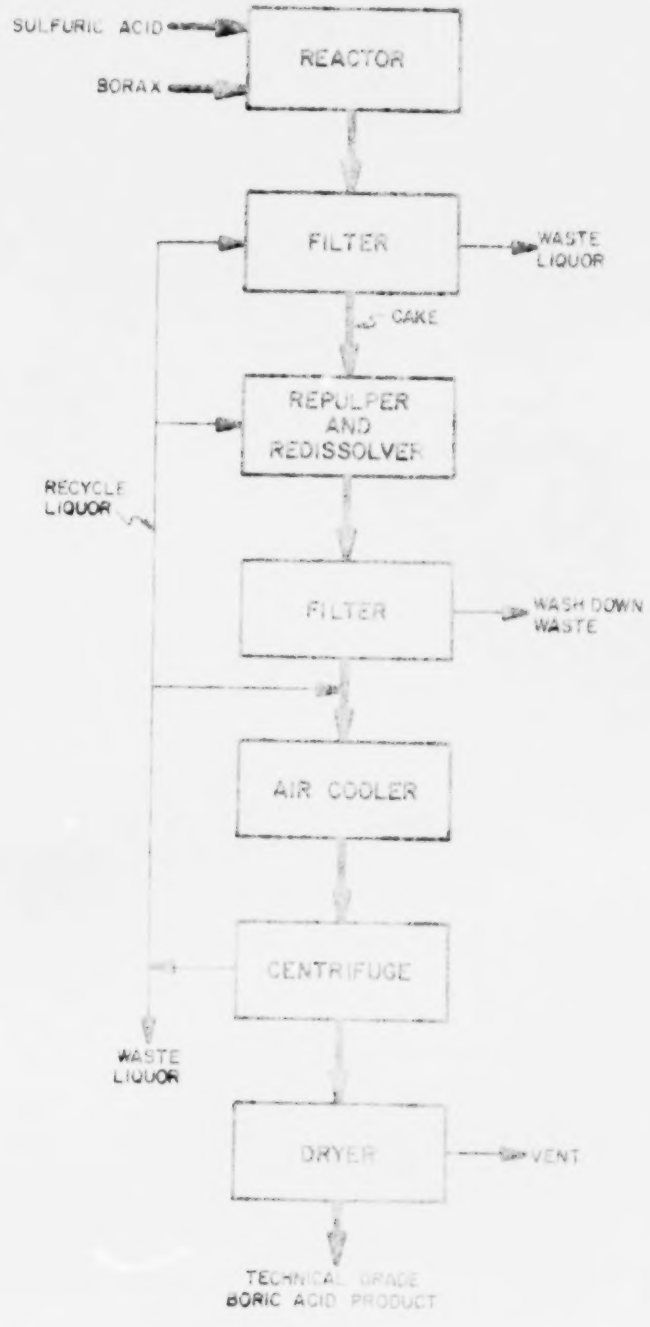


Figure 5
Boric acid manufacture

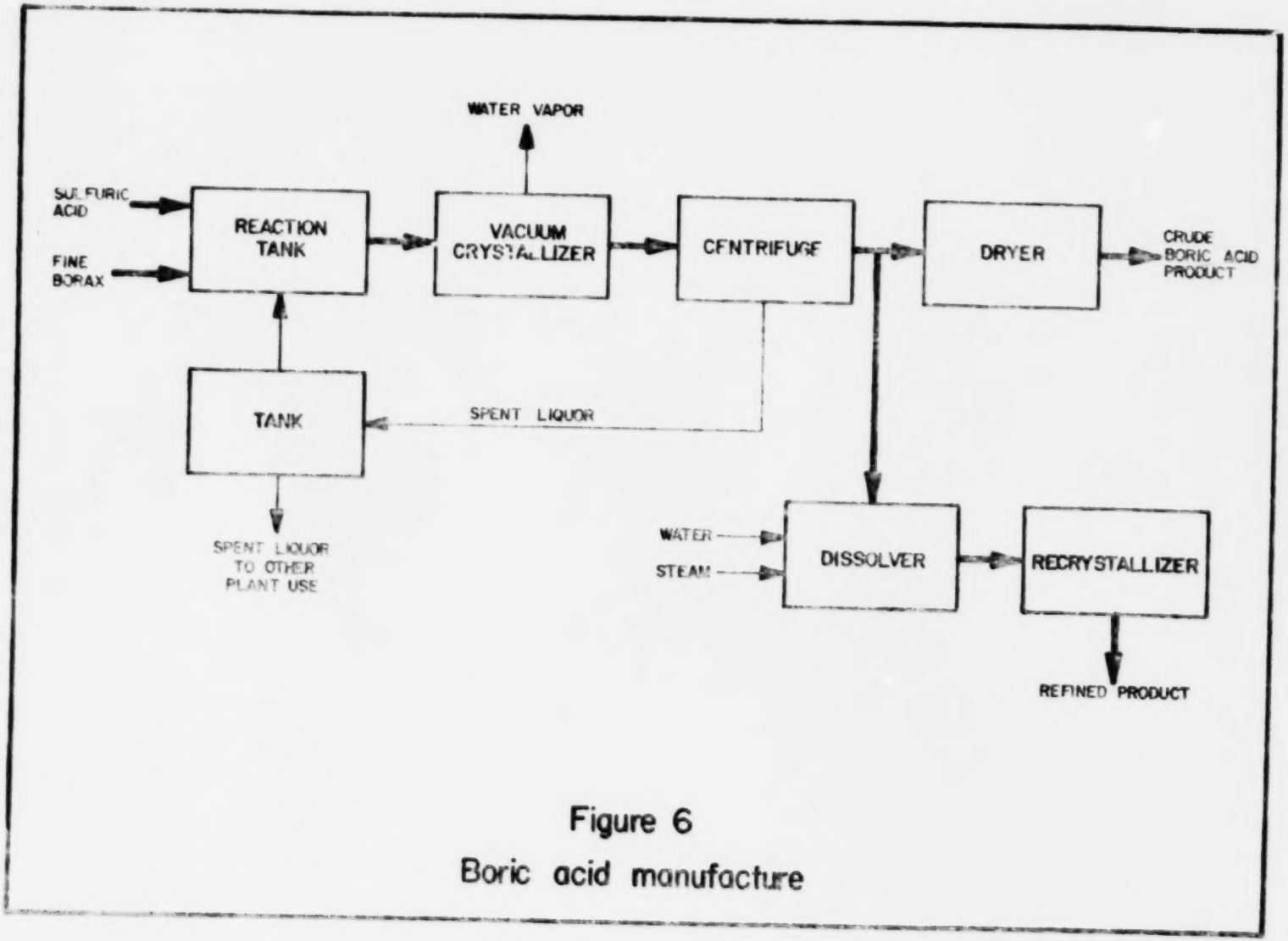


Figure 6

Boric acid manufacture

9. Refractory boron compounds (metal borides, boron carbide, and boron nitride)

The most extensively used methods for producing refractory boron compounds are the following:

(a) The direct reduction of metallic boron with the metal.

(b) The use of reducing agents such as aluminum, silicon, magnesium, carbon, or boron and boric oxide-metal oxide mixtures.

(c) The electrolysis of fused-salt mixtures containing metal oxides and boron oxides.

(d) Deposition from the vapor phase.

The first, and the most common method for making boron carbide, is reacting boron oxide and carbon at 1400-2300C. The use of finely divided carbon such as carbon black speeds the reaction.(5)

The cubic crystal form of boron nitride is made by the synthetic diamond production techniques of high temperatures and high pressures. At this point, its commercial significance is fairly limited; however, it is available.(4)

III. USES OF BORON COMPOUNDS

A. The majority of boron used in the United States is in the form of borax ($Na_2B_4O_7 \cdot 10H_2O$). Figure 7 presents an overall picture of the uses of boron and its compounds. A detailed summary of current boron usage is presented in Table 5.

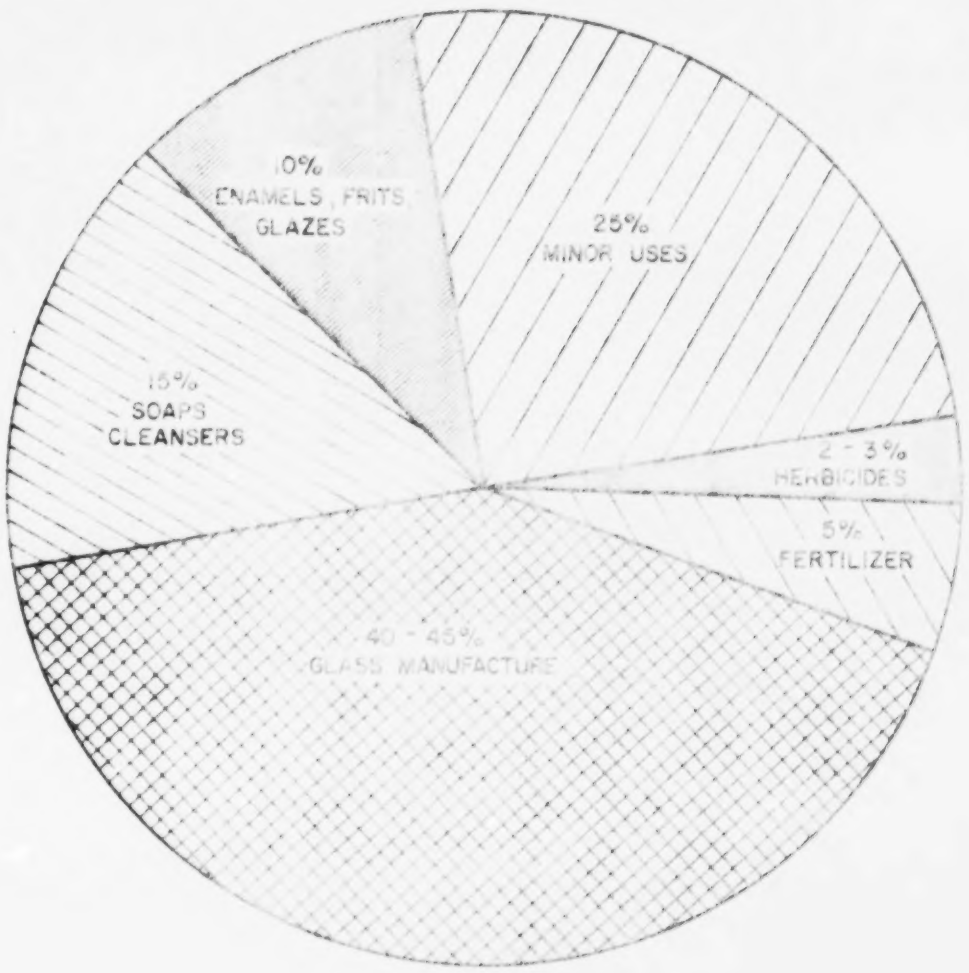


Figure 7

Distribution of Boron uses

Table 5.
(4,5,7,8,9)

| Boron Compound | Use | Purpose | Comments |
|---|---|---|---|
| Elemental boron | Steel | Deoxidizing and alloying element in the form of ferroboron alloy | Dissolves rapidly in molten steel |
| | | Increases hardness of steel | Amount used under 0.003% |
| | Nonferrous metallurgy | Alloying agent | Boron concentration varies from 20% to less than 0.1% |
| Borax<br>Boric Acid and<br>Anhydrous Borax | Manufacture of borosilicate and similar glasses | | $B_2O_3$ essential to impart the low coefficient of expansion required |
| | Optical glass | Gives desired properties including the index of refraction | For glass, to maintain the proper acid-alkali ratio borax is supplemented with substantial quantities of boric acid |
| Borax | Glass containers<br>Novelty ware<br>Structural glass<br>Flat glasses | Aids in the melting, finishing, and forming operation | Borax only used in small amounts |
| | | Enhances color, durability, scratch resistance and strength of finished product | |
| | Cleaning room of enamel plants | Used as an alkali | |
| | Steel and steel plating | Final dip serves as a rust preventative and aid in bonding the first coat to the iron body. | Used alone or in conjunction with other materials. |
| | Leather industry | Mild alkali and preservative | |
| | Detergent, hand cleaner, face cream, cosmetics | Mild alkali and buffer | Used blended with soap<br>Bacterial characteristics and easy solubility in water |

Table 5
(Con't.)

| Boron Compound | Use | Purpose | Comments |
|---|---|---|---|
| Borax and Anhydrous Borax | Manufacture of vitreous enamel frits | Same benefits as in glass manufacture | |
| Borax and Boric Acid | Pottery glazes<br>Colored glass for decoration and marking purposes | | |
| | Other | Improves the resistance to fire of textiles, lumber and other combustible materials | Wood is impregnated under pressure with preservatives such as pentachlorophenol and borate solution for fire proofing in a single pass through a pressure chamber |
| | | Treatment for epilepsy, soothing eyewashes, rectal and colonic irrigations and vaginal douches | Mildly antiseptic and antifungal, but not sufficiently so for most purposes |
| Boric Acid | Manufacture of metal borides, hydrids, master alloys, and as a catalyst in many organic reactions | | Use as a catalyst in air oxidation of hydrocarbons accounted for more than 3% of overall boron consumption |
| Boron Trifluoride | Petroleum Refining | Catalyst in isomerization, alkylation, polymerization, esterification, condensation, cyclization, hydration, dehydration, sulfonation, desulfurization, nitration, halogenation, oxidation and acylation | |
| | Organic Synthesis | Catalyst in the Friedel-Crafts type of reaction, the synthesis of saturated hydrocarbons, olefins, alcohols, thiols, ketones and ethers, in cracking hydrocarbons | |

Table 5.
(Con't)

| Boron Compound | Use | Purpose | Comments |
|---|---|---|---|
| Boron Trifluoride | Preparation of boranes | | Diborane is the only commercial borane of importance being produced at present |
| | Magnesium alloy castings | Protects molten magnesium and alloys from oxidation during casting and a flux for soldering magnesium | |
| Boron Trichloride | Refining aluminum, magnesium, zinc, and copper alloys | Removes nitrides, carbides and oxides from the molten metal | |
| | Soldering flux for alloys of aluminum, iron, zinc, tungsten and monel. | Removes occluded gases, such as hydrogen, nitrogen, carbon monoxide, nitrides, carbides and oxides | Grain growth of aluminum also retarded making it more uniform |
| | Aluminum castings | | Improves the tensile strength and will permit the remelting of the aluminum without substantially changing the grain structure |
| | Manufacture of electrical resistors | | Uniform and lasting adhesive carbon film can be put over a ceramic base by a process that has been developed involving the addition of boron trichloride to benzene at high temperatures |
| | Extinguishing magnesium fires in heating furnaces | | Forms a magnesium chloride film that smothers the fire by preventing air from reaching the metal |
| | High energy fuels and rocket propellants | A source of boron for raising the BTU value | |
| | Catalyst | Suggested use in the polymerization of styrene | Reportedly yields polymers with 3X the molecular weight of those produced with other catalysts |

Table of Uses

Table 5.
(Con't.

| Boron Compound | Use | Purpose | Comments |
|---|---|---|---|
| Diborane | Plastics Production | Catalyst for ethylene, styrene, acrylic and vinyl polymerization | |
| | Rubber Vulcanization | | |
| | Other | Reducing agent<br>Flame-speed acceleration<br>Intermediate for high boron hydrides<br>Doping gas | |
| Boron Carbide | Grinding highly abrasive material | | Self-bonding ability allows it to be molded in graphite and pressed at temperatures up to 2400C into high-density, nonporous shapes |
| | Refractory usage | Jet aircraft parts, rocket chambers and gas turbines | Negative thermal coefficient of electrical resistance |
| | | | Considered a semiconductor |
| Boron nitride | High-temperature abrasive | Properties similar to boron carbide and can be used for the same purposes | When present in the cubic crystal form more stable than diamond in air at high temperatures |

B. Future and Potential Uses

The annual U.S. production of boron minerals and chemicals from raw material supplies has increased steadily at a rate of six to seven per cent per year since the early 1960's. Roughly half of the boron produced is retained for domestic consumption. No new or expanded uses of boron are anticipated to effect the industry in the near future.(5)

Elemental boron has found only limited use as a thermistor material, an intrinsic semiconductor, a photoconductor and a heat-resistant infrared window material. The main obstacle to these uses has been the lack of suitable production and analytical techniques. Progress has been made, however, in elemental boron purification techniques. This should enable greater use of this material in electronic and optical devices.(5)

The demand for glass fibers should increase through the 1970's. In part this will be due to the demand for auto tires, but to a considerably greater extent increased demand can be attributed to the popularity of reinforced plastics. Colemanite is highly desirable in this application as a non-sodium source of $B_2O_3$. One estimate is that the demand for glass fibers in reinforced plastics would increase from 115.4 million kg in 1969 to 412.8 million kg in 1975 and 757.5 million kg by 1980.(2)

A potentially significant demand for borates, possibly colemanite, as a substitute for fluorspar in the basic oxygen-furnace steel manufacturing process has been under consideration for over five years. At the present time this does not appear promising. The substitution of colemanite for fluorspar did not go beyond the pilot plan stage in 1972.(4)

Many companies have shown a great deal of interest in boron industry. Many organic and inorganic boron monomers and polymers have been synthesized and studied. So far no new large-volume boron-containing chemical has emerged and none appears likely.(2)

IV. CURRENT PRACTICES

Borax, colemanite, sodium tetraborate, the various forms of borax, colemanite and anhydrous borax (sodium tetraborate) are sold in bags, barrels, and bulk. Boron trifluoride is included in the "List of Explosives and Other Dangerous Articles". The Interstate Commerce Commission therefore regulates its shipment by land, water, and rail. Boron trifluoride is classified as a nonflammable compressed gas and stored and shipped in I.C.C.-approved compressed gas cylinders. Personnel handling boron trifluoride should wear chemical safety goggles and rubber gloves. Gas masks approved for acid gases or masks with an independent oxygen or air supply should be available in case of emergency. The cylinders used for boron trifluoride should be pretested for leaks with dry air and aqueous ammonia. Leaking containers of boron trifluoride which cannot be corrected should be discharged in a hood and techniques for disposing acid gases utilized.(7)

Boron trichloride is classified by the I.C.C. as a corrosive liquid and is also considered "a dangerous article" in transport. On contact with water or moist air it releases hydrochloric acid so chemical goggles, rubber gloves, and rubber aprons should be used in handling. Leaky containers which cannot be corrected should be disposed of using hood procedures for the disposal of acid gases.(7)

Diborane is classified by the Department of Transportation as a "Class A" poisonous and flammable gas. Diborane and the higher boranes are classified as "dangerous articles" in transport. They are shipped in cylinders pressurized with a diluent gas such as hydrogen, argon, nitrogen or helium. Diborane is highly unstable so no more than 0.1 kg can be shipped in a cylinder. To dispose of diborane the gas is fed into the bottom of a small vessel containing water. The water-diborane reaction produces hydrogen and boric acid.(7)

Procedures for shipping organo-boron compounds vary with the particular compound involved. Amyl borates when contacted with water produce phenols so they are treated as corrosive chemicals. Lower alkyl borates are flammable; methyl, ethyl, and butyl borates have flash points of 0, 32, and 98°F respectively and must be stored in approved areas. Other compounds, such as boron glycol diborate, offer no hazard and may be shipped or stored in any convenient manner.

Organic boron-oxygen compounds readily hydrolyze so they should be stored and transferred in an inert atmosphere. Usually glass containers are used for shipping small quantities; and steel cans, drums, or tank cars are used for bulk items.(5)

## V. ENVIRONMENTAL CONTAMINATION

Boron is a ubiquitous element, generally occurring at concentrations of 10-30 ppm in soils, approximately 0.1 ppm in surface waters and about 4.5 ppm in sea water. Departures from these norms occur only in the very limited areas where natural boron sources are concentrated, such as in certain arid regions of California. Air monitoring data do not measure boron concentration as there is no evidence that it is present in the atmosphere to a significant degree.(9)

In a relatively few areas there is concern about boron concentration. In irrigation waters the boron limit is set at 1.0 ppm. Nuclear reactor materials can tolerate boron only in bare trace amounts. There is also concern about boron concentration in processes where boron dust may be excessive, such as in the mining and handling of borax ore.

### A. From Uses

Virtually all boron-containing materials and products requiring boron compounds in their manufacture constitute potential sources of boron contamination. Little is done to check the boron content of surface and river waters in the U.S. Through the use of boron compounds in detergents and other products, the boron concentration in surface waters can be expected to increase. Since sodium perborate is widely used in Europe in place of the American-type of chlorine-based bleach, the trend toward a build-up of boron concentration in surface waters should be more pronounced there. By following the buildup of boron in European waters it may be possible to establish the point where the agricultural ecology of the U.S. will be upset.(2)

This trend would not be affected by sewage treatment since conventional sewage treatment removes little or no boron. Boron is ingested in the normal human diet, primarily from fruits and vegetables, at the rate of 10 to 20 mg/day and excreted at the same rate with little or no accumulation in the body. Boron in sewage is present as undissociated boric acid.(10)

1. Emissions to the atmosphere (including from production).

Although the incidence of boron and boron compounds in the atmosphere is quite limited, such emissions are known to occur and may be of local concern even if not sufficiently widespread to constitute an environmental problem. Recent analysis of this problem considered potential sources of boron emissions. Emission factors have been determined for individual sources by using: (1) direct observations and plant processing and engineering data; (2) literature; (3) observations of plant operators and others knowledgeable in the field; (4) calculations based on process data; and (5) analytical results where available. Based on the emission factors on Table 6 and the 1972 use figures, estimated emissions to air are given in Table 7.(6)

Details of boron emissions from use pattern are given below.

Glass - The principal sources of particulate matter in the furnace exhaust gases are raw materials entrained in combustion gases and materials from the melt. Particulates expelled from the furnace are the result of many physical and chemical reactions that occur during melting. One factor which appears significant is the furnace production rate - as the latter is increased the quantity of particulates increases disproportionately.

Ceramic Coatings - The principal emissions of boron from the production and use of ceramic coatings occur during the manufacture of the frit. The smelting operation causes the most significant dust and fume emissions. There are also dust emissions from handling the raw materials as they are received, stored, measured, and mixed prior to charging the smelter. The atmospheric emissions of boron during frit smelting consist primarily of oxides in vapor form and in particulates. The magnitude of emissions varies considerably depending upon the amount of boron in the charge, the combination of ingredients, and the type of smelter.

Agricultural Chemical - Emissions to the atmosphere occur principally when the materials are applied as sprays or dusts. Too many factors are involved (air movement, drop size, nozzle type, etc.) to give an accurate estimate of emissions.

Soap and Detergents - Boron compounds in the particulate matter emitted to the atmosphere are reported to be sodium perborate, sodium tetraborate, and sodium borohydride; the particle size ranges from 1 to 10 microns.

Table 6. Air Emission Factors for Boron

| | |
|---|---|
| Mining | 0.5 kg/metric ton boron mined |
| Processing | 14 kg/metric ton boron processed |
| End product uses of boron | |
| Glass manufacture | 35 kg/metric ton boron processed |
| Ceramic coatings | 40 kg/metric ton boron processed |
| Other emission sources | |
| Coal | 9 kg/1,000 metric tons coal burned |
| Sewage and sludge | 28 kg/1000 metric tons sewage and sludge burned |

Table 7. Air Emissions of Boron by Source, 1972

| Source | Source Group | Emission--Metric Tons |
|---|---|---|
| Mining | | 91 |
| Processing | | 2,400 |
| End Product | | |
| | Glass | 1,000 |
| | Ceramic Coating | 472 |
| | Agricultural Chemicals | 1,800 |
| | Soap and Detergents | 13 |
| | Miscellaneous | 500 |
| Other Sources | | |
| | Coal | 4,250 |
| | Sewage and Sludge | 18 |

2. Amount entering waters and earth

The major source of boron entering U.S. surface and ground waters arises from the use of boron-containing laundry products. This source, all of which may be assumed to enter the environment shortly after production, amounts to 15 per cent of the domestic consumption (which is roughly half of the total production). Thus, based on about 600,000 mt total production in 1972 as $B_2O_3$, approximately $1.4 \times 10^4$ mt of boron may be considered to enter the water per year through the use of boron-containing laundry products.

Direct application to the land or crops as fertilizer or herbicides accounts for about seven per cent of domestic usage. This may also be considered as entering the environment immediately upon production. Again, based on 1972 production, approximately $7 \times 10^3$ mt of boron appears to enter the environment per year from this source. Some of this was included on Table 7 in air emissions.

B. From Production

1. Mining

Mining of borax using explosives and its subsequent shipping and handling created a serious dust problem. A three-year, $10 million program to cut down dust emissions at Boron, California was completed in 1972. Nevertheless, the operation is still not satisfactory and efforts to improve it are continuing.[4] There are no detectable emissions in connection with the operation at Searles Lake.

2. Processing

The primary emission from the processing of boron is sodium borate in various degrees of hydration, primarily from 1 to 3 moles of water. Boric oxide, boric acid, and sodium pentaborate are also emitted as these compounds are being produced. Particulate sizes range from less than 1 to 45 microns. Boron emissions vary considerably from plant to plant, ranging from 100 to 2000 mg/kg of product.[6]

The major industrial waste in the boron-related industries appears to arise in the sodium borate effluent from $B_2O_3$ manufacture. This amounts to about 407 kkg per year as boron.

Phosphate rock contains 20-100 ppm boron, but even at a total phosphate rock production of $120 \times 10^6$ mt per year and an average boron content of 50 ppm, the boron effluent (water-borne or landfilled) from this industry amounts to only a few metric tons per year.

C. Inadvertent

These items are considered contaminators only in view of the special applications involved. Boron content of the materials used for construction and the chemicals used in nuclear reactors, for example, must be extremely low. This is because of the high atomic cross section of boron for thermal neutrons. In some cases boron must be removed from water used in the production of nuclear reactor materials. Sea water being used for magnesium oxide production as a refractory material and magnesium chloride brines being processed for magnesium metal when used in connection with nuclear reactors are prepared in this manner. Kunin of Rohm and Haas has developed a boron-selective ion-exchange resin which is available commercially as Amberlite IRA-743.

In the case of irrigation water, a standard of 1 ppm boron has been established. Normally this limit is attained through dilution with other waters. The manufacturers of the Amberlite IRA-743 resin have made recent improvements and now claim that elimination of the average irrigation water can be effected at costs "well below 5 cents per 1,0 cu. m."(11,12)

D. Total Amounts Entering Environment per Year

Total boron released to the environment based on 1972 production and use figures may be summarized by:

| Source | Amount (metric ton) |
|---|---|
| Laundry Products | 14,000 |
| Agricultural Chemicals, Fertilizers | 7,000 |
| Mining and Processing | 3,000 |
| Glass and Ceramics | 1,500 |
| Combustion of Coal | 4,000 |
| Miscellaneous | 2,500 |
| Total | 32,000 |

Of the estimated total of 32,000 mt per year, most ends up in the waters because of the relatively high solubility of all the compounds.

VI. MONITORING AND ANALYSIS

A. Monitoring

Monitoring data on the boron content of U.S. waters is limited. For this reason, results of a survey conducted in Europe is of interest. A study was made for the National Swedish Environmental Protection Board, Uppsala, of boron in Swedish and Norwegian fresh waters. The study began in 1970 and took a year to complete. Regional variations due to differences in geology, land use, and population density were found, but there were only small seasonal variations. The enrichment of boron in aquatic plants was very small compared to that of phosphorus and nitrogen. Sewage water showed a lower boron content than that of England. The mean concentration of boron in Swedish and Norwegian fresh waters was low and close to that of other rivers of the world. The median boron content in 35 samples was approximately 12 micrograms/liter.(13)

B. Analysis

1. Determination of boron in water.

Colorimetric and spectrographic methods have been used to analyze boron in fresh water in concentrations of less than 1 ppm. One of the most useful methods is "the ideation pH" method with which a sensitivity of ± 0.05 ppm boron can be obtained if a 500 ml sample is used. With this method separation or special sample treatment is not required. Detection of the boron by electrometric instead of colorimetric titration is recommended. For use with more than 1 ppm boron, the standard mannitol boride procedure may be used after removing interfering bicarbonate and metal ions.(14)

The analysis of boron in sea water represents a special case. A high degree of precision and accuracy are required because the ratio of boron to total salt content is almost constant throughout the world. Only bicarbonate removal is required for the mannitol boride procedure. Hydroxy organic matter causes low results by complexing the boron.(14)

2. Determination of boron in plants and biological materials.

The boron analysis in plants is important for growth because it is toxic on the one hand and deficiency on the other. The ppm range is normally involved and the best techniques are colorimetric and spectrographic. The treatment of

the sample must be carefully carried out to avoid both loss of boron and contamination from borosilicate glassware. Almost all methods for boron analysis in biological materials involve ignition of the sample which may cause some loss of boron. Contamination with boron from the ovens may be experienced. Spectrographic and flame photometric procedures are more convenient than those requiring extensive treatment after ashing.(14)

3. Analysis of available boron in soil.

Boron is analyzed in soil by boiling a 1:2 soil to water suspension for five minutes in a reflux condenser. The solution phase is separated to determine boron.(15)

4. Detection of boron in airborne contaminants collected in air filters.

To detect boron in airborne contaminants collected in air filters a small portion of the filter is rolled up into a cylinder and placed in a hollow graphite electrode. This portion of the air filter is directly excited by the condensed spark discharge in an oxygen atmosphere. The sample burns, exciting the spectra. A photographic recording is used to interpret the spectra and, when improved precision is required, line intensities are measured with a microphotometer. The limits of detection are 0.1 to 1.0 micrograms. The results obtained from the rapid emission spectrographic method are compatible with results obtained with the more conventional technique of ashing the filter, mixing it with a spectrographic buffer, and exciting it in a D.C. arc.(16)

5. Analysis of boron in air by colorimetry.

In the colorimetry method of analysis, about 1,000 liters of air passes at a rate of two to three liters per minute through four collecting tubes chilled in a methanol-dry ice bath. The collected boron is dissolved in 10 ml. water and added to 1.5 ml. of curcumin reagent solution. The solution is evaporated until the odor of phenol disappears. The residue is dissolved in 10 ml. ethanol and absorbance is measured at 548 millimicrons.(17)

VII. CHEMICAL REACTIVITY

A. Environmental and Use Associated Reactions

Borax solutions, usually a buffer mixture of sodium borate and boric acid, are widely used for pH control in: cutting fluids, detergents and soaps, electroplating, dyeing of natural and synthetic fibers, photographic processing, fermentation, cosmetic preparations, plastics manufacture and vitreous enameling. The pH value of a 0.1M solution of borax is 9.2.(20)

$$Na_2B_4O_7 \cdot 10H_2O \rightarrow 2Na^+ + 2B(OH)_4^- + 2H_3BO_3 + 3H_2O$$

Boron trichloride and boron trifluoride hydrolyze rapidly on contact with water to form boric acid and the corresponding hydrochloric or hydrofluoric acid.

The manufacture of boron-containing mixed fertilizer by the direct action of sulfuric or nitric acids on phosphate rock with fluoride impurities results in a product containing a boron-fluoride complex similar to potassium fluoborate. In Switzerland's Rhone Valley, apricot orchards and vineyards using a certain fertilizer showed high fluoride content in the plants and typical fluoride-induced necrosis of the foliage.(13)

The effect of the environment on biozone and higher borates is given in Table 8. In the case of pentaborate, conflicting data are reported.

B. Aspects with Biological Application

The complexing ability of the boron atom is considered to be the key explanation of its essentiality [illegible]. The exact mechanism of the action is still unknown, and it is the subject of much research. The theory is that the complexing action of boron [illegible] the transport of organic compounds such as sugars in plants. Other mechanisms are also under consideration as an explanation of the effect of boron [illegible] plant enzymes, the interrelationship between boron and [illegible] (plant growth regulator response), nucleic acid metabolism, cellular growth and differentiation, cell wall formation and [illegible] phenolic acid biosynthesis and liquification, [illegible] and respiration, cell wall and membrane permeation, and sulfur [illegible]

Table 8. Relative Stabilities of Boron Hydrides (5)

| Compound | Room temperature, no oxygen | Room temperature, presence of air | Presence of water |
|---|---|---|---|
| diborane | fairly stable, 10% decomposition in presence of hydrogen | spontaneously flammable above 40 C and at room temperature in presence of impurities | hydrolyzes instantaneously and almost quantitatively at room temperature |
| tetraborane | fairly rapid decomposition | not spontaneously flammable if pure | hydrolyzes completely within 24 hr at room temperature |
| pentaborane | (a) stable for years; decomposes slowly at 150 C | spontaneously flammable | hydrolyzes only at elevated temperatures |
| | (b) begins to decompose within 1 hr | | hydrolyzes rapidly |
| hexaborane | decomposes slowly | quite stable; not spontaneously flammable | hydrolyzes completely only at elevated temperatures |
| decaborane | very stable; can be heated for some time at 150 C; noticeable decomposition at 170 C | very stable; not spontaneously flammable; explodes in oxygen at 100 C | hydrolyzes very slowly at room temperature |

of these effects of boron on plant growth probably play some role in its benefits. The primary effects, however, have not yet been determined.(19)

VIII. BIOLOGY

A. Absorption, Excretion, Growth, and Nutrition

1. Humans

The average concentration of boron in the blood and urine of 154 American males of various occupations and ages is 9.85 µgrams per 100 grams and 7.15 mg per liter, respectively.(20) The skeletal tissue contains the highest boron concentration (0.90 ppm) of all body tissues analyzed.(21)

Since boron is widely distributed in fruits and other foods, humans constantly ingest and excrete this element.(22) Conflicting information as to the transcutaneous absorption of boric acid does exist. No increase in boron was observed in the blood of infants maintained on a regimen of boric acid dusting powder "ad lib" for a year.(22) In another study, children using baby powder containing three per cent boric acid had significantly more boron in their blood than the control group.(23)

A fatal case of transcutaneous absorption of boric acid occurred in a seven-month-old male infant being treated for dermatitis with three per cent boric acid powder. The boron concentrations in the bile, intestinal contents and spleen were 20.2, 18.3, and 18.2 mg %, respectively.(24)

After vaginal administration of 40g of boric acid, the serum boron level rose from 0 to 750 micrograms % within 48 hours in a patient with healthy epithelial tissue in the vagina and on the portio, but up to 2150 µgrams % in a patient with vaginitis and erosion of the portio. In patients with vaginitis receiving daily 20g doses of boric acid, the serum boron was a maximum of 850 micrograms % after five days of treatment, and 1900 micrograms % after seven days.(25)

Phenylmercuric borate was not absorbed by the epidermis or cutis in man or rats when applied without a protective dressing.(26)

2. Nonhuman Mammals

Boron compounds are preferentially accumulated by the brain and tumor tissue of animals.(27,28,29) Localization in the brain can be correlated in terms of one parameter obtained from the water/octanol partition coefficients. Localization in the tumor depends also upon the electronic parameter.(29)

An aqueous jelly and two oleaginous ointments containing less than three per cent boric acid were applied to the skin of anesthetized rats, and boron absorption was monitored by measuring boron in the urine. Little or no increase was observed after eight hours if the application was made to intact skin, but when the ointments were applied to damaged skin, four to eight times the control level of boron appeared in the urine. Only 25% of the original boron remained in the ointment after treatment of an enclosed area of damaged skin, but 98% remained in the jelly. In the urine, 25% and 1%, respectively, of the total boron from the jelly and ointment applications were recovered, indicating that a high rate of absorption with inadequate excretion occurred with the aqueous jelly, but the slight absorption from the ointments was followed by rapid excretion.(30)

Sodium methylborate (0.2g B per kg in 2% physiological serum) was injected into pregnant rats on the 18th and 19th days of gestation. Boron penetrated into the amniotic fluid more rapidly on the 19th day than on the 18th, and the diffusion of boron into the amniotic fluid increased as gestation progressed.(31)

The amount of boron in cow's milk varies with the amount of boron in the feed. About one quarter of the total boron is in the cream, the remainder in the skim milk.(32)

3. Plants

As shown in Table 9, nutritional requirements for boron vary greatly. Boron deficiency in plants induces severe symptoms. These include cessation of root and leaf growth, necrosis of leaf primordia and primary root tips, spongy mesophyll layers of leaves, necrosis of stem and leaf phloem, bark splitting, reduced pollen germination and pollen tube growth, reduced fluorescence, abnormal cell differentiation, reduced growth, and death if the deficiency is not corrected. Normal growth and development usually resumes when boron is added to the growth medium.

Boron is absorbed by the roots of the plant and translocated to the leaves, where it occurs in highest concentration. In a study on sunflower

Table 9. Diagnostic Criteria for Boron Nutrition of Field and Vegetable Crops Based upon Hot Water Extraction of Soil Boron (169)

| Boron Content of Soils for Optimum Growth | | |
|---|---|---|
| 0.2 μgram of B/gram | 0.3-0.5 μgram of B/gram | 0.5 μgram of B/gram |
| Small grain | Tobacco | Apple |
| Corn | Potato | Alfalfa |
| Soybean | Lettuce | Clovers |
| Field beans | Beets | Beets |
| Celery | Onion | Turnips |
| Potato | Cucumber | Cruciferae |
| Grass | Olive | Asparagus |
| Flax | Pecan | Radish |
| | Orange | Celery |
| | Sweet potato | Rutabaga |
| | Peanut | |
| | Carrot | |
| | Pear | |

boron accumulation required nitrogen in the nutrient solution. Once in the leaves, boron was not transported to other parts of the plant.(32) As boron in the nutrient solution increased, boron in the leaves increased in the carnation, Dianthus caryophyllus, but not in the reproductive organs.(33,34) Figure 8 relates boron concentration in plant tissues to the concentration in soil solution.(35) Similar results were observed in studies on tobacco, onions,(36) and birch.(37)

Borate absorption by excised sugarcane leaves occurred in a two stage transport system. The first stage is a rapid, reversible influx into the mesophyll cells of the leaves, followed by a slower, irreversible accumulating phase. Stage two consists of three absorptive reactions. The first two reactions involve active transport of borate across the cell membrane; the third carries the borate across the vacuolar membrane. Calcium is essential for maximum boron uptake, and all three reactions are inhibited by hydroxide ions. Reactions one and two are apparently coupled to the electron transport system. The third may be linked to oxidative phosphorylation.(38)

Phenylboric acid, which is split into phenol and boric acid by horse radish peroxidase and oxygen, promotes the lengthening of roots in Phaseolus vulgaris primarily by stimulating the rate of cell elongation. Phenylboric acid also stimulated the initiation of xylem development and the full elongation of epidermal cells at a greater distance from the apex than in controls.(39)

4. Microorganisms

The thermostability of Paramecium caudatum at 40 C was increased by the addition of 0.01 and 0.05 per cent boric acid to Losina-Losinsky saline solution at a pH of 7.0-7.2. At pH 6.4 or lower, however, the addition of boric acid caused a decrease in the thermal stability of the ciliates.(40)

B. Biochemistry

1. Humans

No requirement for boron in humans is known. Since boron is excreted from the body very slowly, accumulation in the tissues is likely to occur.(41) The long term effects of drinking water high in boron (4.6 mg per liter) on the

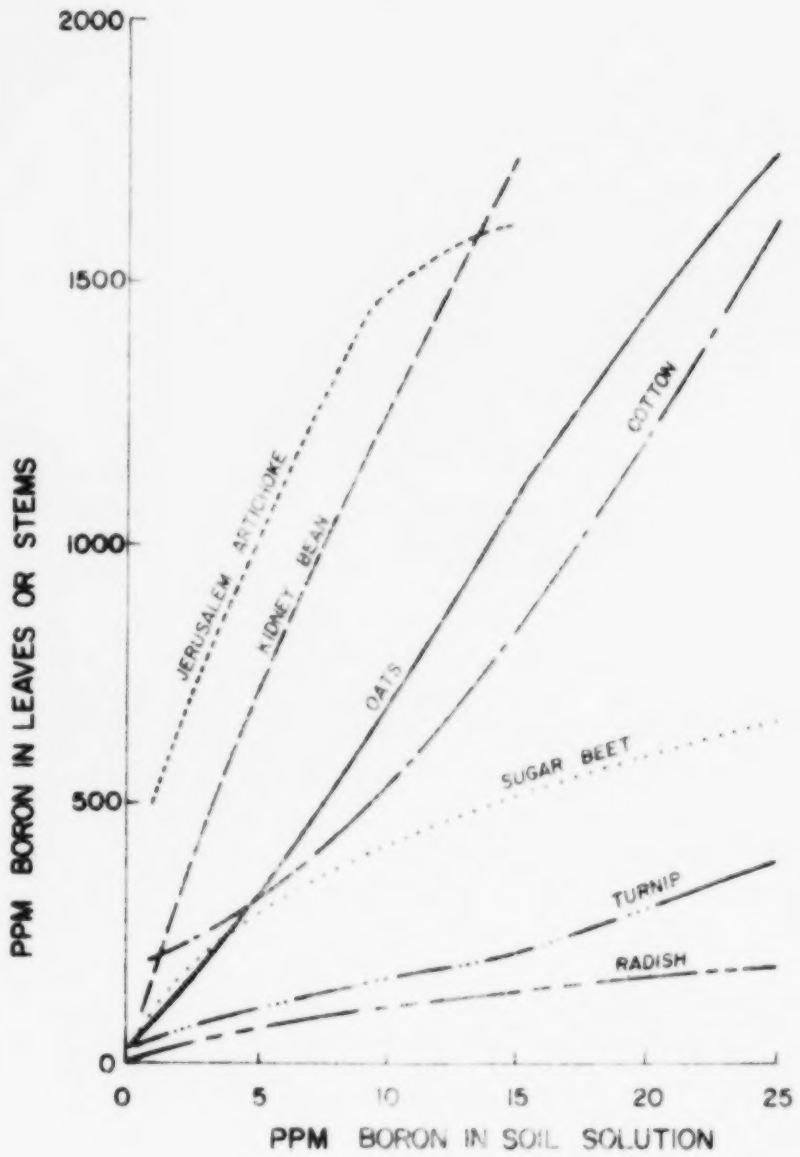


**Figure 8**
**Boron concentration in plant tissues related to concentration in soil solution**

gastrointestinal tract were studied in 288 persons. In people drinking high-boron waters, the incidence of hypoacidity doubled in adults, and enterokinase activity in feces of children was 25% of that in persons drinking low boron water.(42)

Borates cause noncompetitive inhibition of nonspecific ester hydrolysis by chymotrypsin, perhaps by interacting with the free electron pair on an imidazole moiety at the active site. Changes in ionic strength (0.06 - 0.4) do not significantly affect the inhibition, but changes in pH do.(43) Aryl and(44) alkyl boronic acids act as competitive inhibitors of $\delta$-chymotrypsin. The ionic borate group apparently interacts with histidine and/or imidazole residues at the active site, and the organic residues interact with hydrophobic sites. n-Hexylboronic acid had the strongest inhibitory effect of the n-alkylboronic acids studied.(45)

2. Nonhuman Mammals

Boric acid and its salts affect diverse metabolic pathways in animals. In rats fed a low-borate diet (0.001 ppm boron), liver RNA synthesis as measured by $^{14}$C-orotic acid and $^{14}$C-uridine incorporation is stimulated by the intraperitoneal injection of borate. Feeding of 1 ppm boron diminished this effect. The activity of rat liver DNA-dependent RNA polymerase was stimulated *in vitro* by $10^{-6}$ to $10^{-5}$ M borate, but higher concentrations were inhibitory.(46)

Inhibition of oxygen utilization in the brain by boric acid and sodium metaborate can be significantly alleviated by the presence of glucose and pyruvate in the medium.(28) In the rat, boric acid was found to inhibit glucose-6-phosphatase, phosphoglucomutase and phosphohexose isomerase in the liver, brain and kidney, except that kidney phosphoglucomutase was stimulated by borate.(47) Borate competitively inhibited glyceraldehyde phosphate dehydrogenase in rat and guinea pig liver homogenates, causing fructose-6-phosphate and fructose-1, 6-diphosphate to accumulate. Lactate dehydrogenase was not affected by borate.(48) Anaerobic glycolysis in guinea pig erythrocytes was inhibited by addition of borate to the blood, and methemoglobin increased substantially.(49) The inhibition of methemoglobin reduction by borate, which is greater in species other than in rats, guinea pigs and rabbits, may be alleviated by the addition of $NADH_2$.(49) The loss of activity may occur via glyceraldehyde phosphate dehydrogenase inhibition. The ratio of NAD:$NADH_2$ increases in the presence of borate

indicating [illegible] $NAD_2$. The NADPH system was not as greatly affected by boron as the NADH system.[49]

Changes in the ESR spectra of heme and non-heme iron complexes were observed in livers of rats with boric acid intoxication.[50] A sharp decrease in the electron spin resonance signal of pigment 450 in the respiratory chain of mitochondria was also noted.[50]

The addition of 2-4 mg per liter or more of boron to the drinking water of rats resulted in increased gastric secretions, free and total gastric hyperacidity and inhibition of beta-glucuronidase activity.[51] In rabbits receiving daily gastric administration of 100 mg per kg calcium borate, a slight increase in [illegible] and free hydrochloric acid in the gastric juice was observed. Inhalation [illegible] mg/2 hours/day for 10 weeks resulted in an increase in urinary excretion of [illegible] proteins.[52] The beta-oxidase activity of [illegible] in kidney acetone powder was increased 290% in 5-100 mM borate buffer. The borate effect was mainly due to stabilization of the enzyme.[53]

Borate increased the adenosine activation of rat liver dephosphophosphorylase.[46] A mixture of borate and L-serine inhibited gamma-glutamyl transpeptidase in various tissues and tissues (kidney, liver, spleen, uterus, [illegible], intestine, heart, [illegible] and testicles). Intravenous injection of L-gamma-glutamyl-alpha-naphthylamide, followed by borate-L-serine treatment resulted in a decrease in [illegible] and increased amounts of [illegible] in the urine.[54]

Tetraphenylboron [illegible] protein synthesis.[55] In isolated rat liver cells, the administration [illegible] of $^{14}$C-alanine, glycogen concentration and the effect [illegible]. The incorporation of $^{14}$C-leucine into protein was lowered, as were the activities of glucose-6-phosphate phosphohydrolase and lactate dehydrogenase.[56] In rat liver mitochondria, TPB exerted a powerful uncoupling of oxidative phosphorylation, [illegible] electron transfer, calcium transport, and $Ca^{2+}$-dependent [illegible] stimulated ATP hydrolysis.[57] Sodium TPB inhibition of liver mitochondrial [illegible] is overcome by the increased rate of hydrolysis of [illegible]

The antitrichinellic action of TPB most closely resembles that of tetramethylammonium triethylcholine and phenol. In the biventer cervicis muscle of the chick, TPB increases acetylcholine release and also exerts a weakly anticholinesterase effect.(59) TPB exerts a blocking action on acetylcholinesterase in guinea pig smooth muscle.(60)

Organic derivatives of boric acid exert a wide variety of effects on diverse tissues. o-Methoxybenzene-boronic acid exerts a peripheral hypotensive action, which is not accompanied by a hypnotic effect. This compound stimulates an increase in cardiac contraction and increased cerebral blood flow.(197) Pentaerythritol di-(p-methylbenzene boronate), p-methylbenzeneboronic acid, and methyl-p-methylbenzeneboronate are not hypnotic, but enhance the hypnotic effects of chloral hydrate and hexobarbital.(148) The first drug causes an increase in arterial blood pressure, but it acts as a peripheral dilator and depresses cardiac contractile activity, and inhibits the hypertensive action of exogenous and indirect agents.(148) o-, m- and p-tolylboronic acids become localized in the cerebrum; for example, one hour after intraperitoneal injection of sodium-p-tolylboronate, the boron content in the cerebrum was six times that of the blood.(149) Spasmolytic activity of seven arylboronic acid compounds was studied in isolated guinea pig duodenum. The substitution of one hydroxyl group in boric acid by a methyl-benzene group conferred spasmolytic activity. o-Methoxybenzeneboronic acid differed from other derivatives in that it exerted a specific parasympathetic spasmolytic activity and no neurotropic activity.(201) Some of the derivatives exerted an antiacetylcholine effect on the uterine tissue of virgin rats.(61)

Boronic acid derivatives produce changes in tissue amino acid levels in the rat by inhibition of pyridoxal-dependent enzymes such as aminotransferases(62) (63) and histidine decarboxylase.(64) Tissue histamine levels were greatly reduced by injection of decaborane (15 mg per kg). Histamine was reduced in liver, kidney, stomach, brain and urine, but not in heart. Brain levels fell 50% and were still depleted one week after injection, whereas the stomach depletion lasted only 48 hours.(64) Changes induced by pyridoxine deficiency in rat are accentuated by intraperitoneal boron injection (20 mg per kg).(65)

However, aspartate aminotransferase (AAT) activity is greater in the tissues of pyridoxine-deficient rats, and decaborane does not significantly affect it. Decaborane does inhibit AAT in the liver, heart, brain, and kidneys of normal rats. Lactate dehydrogenase is moderately inhibited by decaborane in the heart and kidney of normal and pyridoxal-deficient rats and in the brain of normal rats.(63,66)

Borohydrides readily reduce the double bond of the Schiff base formed from cytochrome oxidase.(67,68)

3. Nonmammalian Vertebrates

Boric acid produced malformation of the posterior extremities of the chicken embryo, possibly by interfering with the process of extension of the collagen fibers in the cartilage.(69)

Vitamin C was useful in protecting the tadpoles of Rana temporaria from the toxic effects of phenylmercuriborate.(70)

p-Nitrobenzenediazonium fluoroborate and its trimethyl derivative are potent inhibitors of the carbamyl-choline-induced depolarization of the electroplax and also of acetylcholinesterase. These organoboron compounds are believed to form covalent bonds with the acetylcholine receptor and esteratic sites on the electroplax.(71)

4. Plants

The essentiality of boron to higher plant reproduction, growth and metabolism is firmly established. Boron deficiency symptoms are browning and spotting of leaves, chlorosis, necrosis and finally death. No single specific role has been found for boron; it in fact seems apparently exerts many effects on a variety of metabolic sites. The following summary of boron biochemistry in plants is primarily based on a review article by Lewis.(66)

Boron apparently controls plant metabolism by inhibiting certain key enzymatic reactions in plants. Several sites of inhibition occur in carbohydrate metabolism. Effects of boron deficiency which may be explained via effects on carbohydrate metabolism are increased starch accumulation, increased peroxidase activity, leading to an accumulation of polyphenol compounds and an increase in phenolic acids and indoleacetic acid (IAA). An increase in cell wall products of altered composition were also observed. Reproduction and growth are adversely affected.

Starch accumulates as a result of alleviation of borate inhibition of starch phosphorylase, reducing the amounts of free reducing sugars. Uninhibited activity of the pentose shunt permit increased hexose metabolism via the pentose shunt. The products from this cycle are converted into polyphenolic compounds, which are normally complexed by borate and not further oxidized. Under conditions of borate deficiency, oxidative enzymes (including catechol oxidase, xanthine oxidase, horseradish peroxidase, tyrosinase and alcohol dehydrogenase) convert these compounds to toxic polyphenolic acids. IAA accumulates due to its reduced oxidation due to the presence of other polyphenolic substrates. Reduced polymerization of phenolic compounds into lignins also occurred.

Nucleic acid metabolism and protein synthesis are also disrupted by boron deficiency. Boron controls RNAse activity by inhibition or sequestration. In boron deficient plants, RNAse activity is greatly increased and RNA content greatly reduced. DNA synthesis, RNA synthesis, and aminoacyl tRNA levels are maintained, but rate of protein synthesis is decreased, and an increase in free amino acids and total nitrogen content in plants occurs. Growth and reproduction are almost certainly aborted in boron-deficient plants due to inadequate protein synthesis resulting from disturbed nucleic acid metabolism.

In boron-deficient plants, kinase activity is reduced and ATP levels are quite low. The reduction of available ATP also prevents the normal operation of energy-requiring synthetic reactions, including chlorophyll synthesis and protein synthesis.

Boron promotes the uptake and translocation of carbohydrates and reduces nitrogen absorption in nitrogen sufficient plants.(220) Xylem proliferation is stimulated by boron. Borate ions in the medium clearly inhibited chloride absorption, but not iodine uptake, in Lemna minor.(73) Boron fertilization reduced water loss in sugar beets throughout the entire vegetative period, and the addition of lime prevented the toxic effect of too much boron and actually increased the boron requirements.(74) The accumulation and disposition of thiamine to the cotyledonous shoots of lupine was facilitated by boron.(75)

5. Microorganisms

No nutritional requirement for boron has been established in microorganisms, but borates added to the medium produce definite metabolic effects, primarily inhibitory and toxic.

In yeast in sucrose solution, boric acid favored anaerobic respiration at the expense of aerobic. The number of cells rich in glycogen decreased with one to two per cent boric acid, but little effect was observed with four per cent probably due to a larger proportion of the more active orthoboric acid in more dilute solution.(76) Fructose-1, 6-diphosphate and ADP accumulated in boron-toxic cultures of Saccharomyces cerevisiae, whereas phosphoglyceric acid and ATP levels decreased. This effect was explained by the uncompetitive inhibition of aldolase by boric acid.(38) Yeast alcohol dehydrogenase was also inhibited by borate.(77) Borate buffer also influenced the production of 5'-nucleotides via the autodegradation of intracellular RNA in yeast.(78)

In fungi, o-diphenol oxidase was competitively inhibited by borate.(46) Borax inhibited the formation of HCN by a normally cyanogenic isolate of the snow mold of alfalfa.(79) Boric acid exerted a toxic effect on fungi by preventing $O_2$ uptake and $CO_2$ evolution.(38)

Erythromycin, produced by Streptomyces, is known to lose its biologic activity in borate buffer solution by the formation of complexes involving dihydroerythromycin.(80) Boric acid prevents the incorporation of separately-formed sugars into erythromycin by complexation, and also causes the synthesis of structurally-changed sugars which result in biologically inactive erythromycin.(81)

sodium borate inhibits the decomposition, presumably by microorganisms, of two protein hydrolysates attractive to the Mexican fruit fly.[82] Borate sensitivity in staphylococci correlated well with lysozyme and α-toxin production in the coagulase-positive strain.[83]

Boric acid had an inhibitory effect on RNA-dependent DNA polymerase of avian oncogenic viruses and, to RNA-dependent RNA polymerases of various RNA viruses.[84]

c. Therapeutic Uses

1. Antiseptic

Boric acid, as well as simple inorganic boron compounds, has a variety of [illegible] properties. Three per cent and two per cent solutions of boric acid [illegible] the growth of Escherichia coli, Staphylococcus aureus, and Proteus vulgaris for over a week, although no bactericidal activity was observed.[85] Boric acid is a useful preservative of urine specimens. A three per cent boric acid solution preserves the urine specimen for up to 24 hours.[86] Of 235 strains of coagulase-positive S. aureus, 221 (94%) were inhibited by $1.5 \times 10^{-8}$ M sodium borate. Only 6 out of 57 (10.5%) of the coagulase-negative strains were inhibited at this concentration. Four of the six strains were [illegible] to mercury, and one was a hospital pathogen.[83]

The [illegible] action of boric acid is increased in the presence of some polyhydroxy compounds, and most notably agents which complex with boric acid such as lactic acid, [illegible], and basic agents, such as salicylic acid, oxalic acid and pentachlorophenol [illegible] with boric acid and exhibit strong synergism. Penicillium notatum, P. expansum, P. glaucum, Aspergillus niger, and Mucor [illegible].[88]

Phenylmercuric borate [illegible] has been found useful in treatment of various mycotic [illegible], especially of acid soil (e.g., Trichophyton cutaneum, pityriasis versicolor), generally of acid soil (e.g., 0.06% phenylmercuric borate) and fungous [illegible] (0.05% phenylmercuric borate) or two marketed preparations.[89,90] [illegible] with 3% hexachlorophene in a bland emulsion [illegible]

The antimicrobial action of Remanex, a commercial mixture of the two compounds, was much more effective upon Streptomyces sp. than either of its components alone.(92)

Orthoanisyl boric acid, exhibiting a low toxicity and readily eliminated, serves as a nonhypnotic sedative which reinforces the action of hypnotics and anticonvulsants.(93) Pentaerythritol di-(p-methylbenzeneboronate) acts as an anticonvulsant for Metrazol and electroshock seizures but has no effect on strychnine convulsions.(61)

Tumor-specific boron-containing compounds have been evaluted for use in tumor therapy by neutron capture techniques. 3-amino-4-carboxybenzene boronic acid, m-boronosuccinanilic acid and sodium octahydrodecaborate,(94) as well as boron-labelled antibodies and elemental boron,(95) have been tested as neutron targets.

An 0.5% solution of levepinephrine borate enhanced the hypotensive response to pilocarpine. Maximum response occurred with a 4% solution.(96)

2. Nonhuman Mammals

A three percent solution of boric acid was the most effective therapeutic agent in treating Thelazia infestations in 250 calves.(97)

Phenylmercuric borate at three concentrations (0.125%, 0.25%, and 0.50%) was effective in inhibiting dental caries in fissures and smooth surfaces of teeth in Osborne-Mendal rats fed a high-sucrose diet.(98)

Borotungstate was inhibitory to mouse sarcoma-leukemia virus infection of cultured cells.(99) Absolute control of an experimental sarcoma in mice was attained by boron thermal neutron interaction.(100)

3. Plants

Treatment with boric acid protects plants against insect and fungus infection. The two-toothed longhorn beetle, Arhecdontus tristis, in sapwood kahikatea, Podocarpus dacrydioides, did not survive a treatment of 0.142% or more boric acid.(101) Boric acid solutions greater than 1.09% were effective against several termite species: Nasutitermes exitiosus, Coptotermes lacteus, and C. acinaciformis.(102) Boric acid was useful as a stomach poison in killing the wood-destroying larvae of Hylotrupes bajulus in wood not exposed

to wax.[103,104] When boll-weevils are fed $^{10}$B-boric acid and irradiated with neutrons, a ten-fold increase in mortality and two-fold increase in sterility occurred in the adults.[105] The presence of McPhail traps baited with a cotton-seed hydrolysate and borax reduced infestation of navel oranges and mangoes by the Mexican fruit fly (Anastrepha ludens) by 68% and 98% respectively.[106]

Boric acid and borax are both cleared by the FDA for post-harvest use on citrus fruits as fungicides.[107] An 0.2% solution of boric acid prevents attack of wool rotting fungi such as Lycrus brunneus Steph,[104] Merulius lacrymans, Coniophora cerebella, Lezites trabea, and Lentinus lepideus.[103] Mold growth was completely inhibited by 2.5% boric acid or borax.[103]

Application of boron-calcium or borax-calcium naphthalene acetamide foliar sprays significantly reduced the number of cork spots per fruit in a Golden Imperial apple trees. The number of spots on fruit flesh and peel decreased as the boron and calcium content of the leaves increased.[108] Borax applications were effective in preventing Fomes annosus (root rot) infection in several species of conifer. Dry powder applications prevented root rot in Jeffrey pine stumps[109] and white fir stumps.[110] The growth of mycelium was prohibited by 75 ppm borax; germination of conidia, by 65 ppm; and basidiospore formation at 90 ppm.[111] Application of 660 ppm total anhydrous borax to oven dry wood of the loblolly pine (Pinus taeda) raised the pH of the wood from 4.8 to 7.6-8.1 and prevented the growth of Fomes annosus.[112]

Tetraboron application was only partially effective in controlling Fusarium in tomatoes grown in [illegible].[113] A one per cent solution of borax was effective in inhibiting the growth of Helminthosporium oxalicum and Helminthosporium cynodontis, the most active microorganisms infecting Egyptian cotton.[114]

## IX. ENVIRONMENTAL EFFECTS

### A. Environmental Content, Transport, Contamination

Boron exists in several forms in the soil. Boron is present in organic matter, in various soil minerals such as tourmaline, and in the soil solution in equilibrium with boron adsorbed on the surfaces of soil particles. The bulk of the total boron comes from soil minerals, hence the soil boron content is primarily related to the parent material of the soil. Soils from marine shales are particularly rich in boron, with sedimentary soils next, followed by igneous. Small and variable amounts of boron are found in soil organic matter. This boron becomes available to plants as it becomes mineralized and redistributed in the soil-water system. In soils above the detrital cone of the Danube in Hungary, boron was shown to accumulate in the upper soil levels, which contained 1.67 to 3.06 times the amount of boron found in the parent material of the soil. (182)

The boron in soil solution and the boron adsorbed to soil minerals is in an equilibrium dependent upon the boron concentration of the solution (particularly the borate ion), pH, organic matter content, and the number of active adsorption sites per unit weight of soil. Although plants absorb boron directly from the soil solution, it is the adsorbed boron which provides a source of boron to maintain the soil solution level.

The adsorption sites for boron are associated with broken silicon-oxygen and aluminum-oxygen bonds exposed at the edges of aluminosilicate metals, with surfaces of amorphous hydroxides such as allophane and hydroxyaluminum and iron compounds, with magnesium hydroxide coatings and clusters that form on the exposed surfaces of ferromagnesian minerals and micaceous layer silicates in arid soils, and with sesquioxide coatings on the surfaces of clays. Volcanic ash soils absorb the highest amounts of boron. (109, 183)

Boron adsorption occurs independently of pH in the acid range, with increased absorption in the alkaline range, and maximum absorption at pH 9.0. These pH effects suggest that it is molecular boric acid that is adsorbed under acid conditions, while it is the borate ion which is adsorbed at the pH approaching 9.0.

Boron adsorption takes place independently of concomitant adsorption of other anions. Adsorbed boron tends to leach relatively easily from soils. In a study of the heath podzol and gray-brown soils in Schleswig-Holstein, the low leaching of the heath podzol indicates the relatively high capacity of raw humus to bind boron.(184) Water-soluble boron is usually determined by a hot water extraction technique or a saturation-equilibration method followed by vacuum extraction.(169) Significant correlations were found between hot-water extractable boron and salinity,(185,186) organic matter content,(182,183,186,187) pH(183) and fineness of soil texture.(187)

Liming of two acid soils with calcium carbonate decreased boron mobility.(188) Lime depresses soluble soil boron reserves.(34, 189)

Seasonal variations in the boron content of the waters of Sweden and Norway were small.(190) Increased levels of boron were observed in rainfall in the southeastern U.S. during the winter months.(191)

In sandy soil, twenty pounds of borax per feddan is toxic to berseem. In loamy soil, fifty pounds per feddan is required to produce toxicity symptoms. Heavily calcareous soils offset the boron toxicity. In saline and alkaline soils, boron toxicity could be corrected by leaching and replacing sodium with calcium.(192)

The soil content of boron may not only be altered by application of boron-containing fertilizers, which leach in varying degrees, but also by airborne boron, primarily from human activities. In urban garden soils of Scotland, the water-soluble boron levels were two to three times the levels in arable rural soils.(193) In "fly ash", boron (with manganese or aluminum) is the toxic substance.(194)

In certain industries, such as boron carbide and boron fertilizer industries, workers are exposed to air pollutants and chemicals which may produce a chronic health problem.(12, 13, 195) The maximum permissible level of calcium borate in the air in the industry should not be more than 10 mg/m³ of air.(52)

Due to crop sensitivity to boron, the levels of boron in waters used for irrigation should not exceed the critical boron concentration for the particular crop species as follows:(169,196)

| Crop Species | Critical boron Concentration (gram B/ml) |
|---|---|
| Sensitive | 0.3-1.0 |
| Semitolerant | 1.0-2.0 |
| Tolerant | 2.0-4.0 |

A serious criticism of this type of evaluation is the lack of provision for soil type, irrigation management and climate.

Sources of boron introduced in waters are soil minerals, rainfall, industry, and sewage effluents. The salinity of surface waters in the United States have boron concentrations ranging from 0.1 to 0.3 gram B/ml.(169) In a study of boron content in rainfall in two sites in Mississippi and one in South Carolina, the boron concentration was 10 ppb, and the input of boron by rainfall amounted to 62.7-74.2 grams per hectare for a one year period.(19)

The Santa Ana River basin in southern California is a good example of the effects of urbanization on the water supply. The volume of return flow from irrigation is steadily decreasing while the input from municipalities is increasing. The waste discharge accounts for 0.75-1.50 grams of B/ml depending upon the city and the season. As much as 50% of the boron in effluents originates from household use such as in laundry detergents.(169) In limiting the inputs from sewage effluents, the permeability rainfall must be considered, as well as the type of soil. The hazard of boron is essentially eliminated if the effluent percolates through the soil.

A. Bioaccumulation and Content

1. Human

The average urine and blood content of boron in several human populations and geographical locations were 3.4% and 1.7% per liter and 7.1% and 1.7% per liter of urine.(20) The boron-phosphorus ratio in urine and the phosphate ratio appeared to be strongly related to dietary boron and may be a very convenient boron/blood boron ratio.(198)

2. Mammals

Boric acid accumulated in the brain after repeated injections.(27)

Boron, which appears to be a normal constituent of cow's milk, increased from 270 to 630 micrograms per liter on the average in the milk of cows fed 300 mg sodium tetraborate per day for two weeks. The concentration of boron did not vary with the amount of milk produced.(32) About 25% of the total amount of boron in cow's milk was found in the cream; 75% in the skim milk.(32)

3. Plants

The boron contents of plants depend not only on their taxonomic position, but also on the amount of soil boron and degree of availability.(199) On the ninth day after boron treatment in sand culture, groundnut accumulated excessive boron in the basal, mature middle and apical developing leaves (2.51, 2.86 and 2.62 mg per gram dry weight).(200) Boron levels in 22 species of aquatic macrophytes from a reservoir ranged from 1.2 to 11.3 ppm dry weight. Boron uptake studies on the swamp plant, Typha latifolia, however, showed no significant correlation between boron in the soil and plant tissue levels.(191)

Boron concentrations in plants may vary with the season. Typha latifolia exhibited maximum boron uptake during early spring growth.(191) The leaves of the trees in an oak - hornbeam forest (Quercus petrae, Q. cerris, Carpinus betulus, Acer campestre, Cornus mas, Crataegus oxyacantha and Ligustrum vulgare) accumulated boron and calcium up to three times the levels found in the leaves in the spring.(202)

Disease stress may affect boron accumulation. The boron content of a clubroot-sensitive cabbage cultivar was higher than in a clubroot-resistant one. As clubroot infection in the sensitive plants increased, the boron content increased even more. In the resistant plants, however, the boron content initially increased slightly and then decreased during clubroot infection.(203)

Boron can affect the accumulation of other elements in plants. The dry matter from vineyards and apricot orchards in the Hunza Valley in Kashmir had a fluoride content up to 600 ppm was due to a boron-containing fertilizer. A particular boron-fluoride chemical combination of unknown composition, similar to $KBF_4$, is formed in the fertilizer during the manufacturing

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the urine by the polyvinyl alcohol-borate-iodine reaction[122] since borates are rapidly excreted by the kidney in largely unchanged form.[35]

Hypoacidity in adults and decreased fecal enterokinase activity in children were observed in 288 persons drinking high boron water for prolonged periods.[42]

Decaborane in low doses is known to have severe disruptive effects upon behavior.[124] The symptoms include depression, catatonia, muscular fasciculations, and occasional convulsions.[125] Little or no central nervous system damage has been reported as a result of toxicological research on boranes.[126]

Boron trifluoride is corrosive to the eyes, skin, and mucous membranes, and will cause burns on the skin similar to, but not as penetrating as, hydrogen fluoride. Boron trichloride and boron tribromide are also very corrosive. These effects are apparently due to hydrolysis of the boron trihalides to the halogen acids and not to boron.[127]

Organic derivatives of boric acid potentiate the sedative action of hypnotics.[61]

2. Chronic Toxicity

Workers exposed in the packaging of boron fertilizers complained of poor appetite, nausea, and loss of weight.[34] Aerosols and inadequate shielding in the boron refining industry may create a risk of pneumoconiosis and pneumosclerosis.[128]

Vacuum drying of boric acid in the fires and aerosol of boric acid production were two to five times permissible levels, sulfuric acid fumes were above normal in 64% of the samples, and high temperature and humidity prevailed. Medical examinations of the workers revealed alterations of upper respiratory tract mucosa, arthralgia and artralgia. The percentage of gynecological diseases was rather high.[42] Men exposed to boric acid production showed weakened sexual activity, decreased seminal volume, low sperm count and motility, and increased seminal fructose.[129]

Inhalation of the dust from colemanite ore (a mixture of $2CaO \cdot B_2O_3 \cdot 2SiO_2 \cdot H_2O$ and $CaO[B(OH)] \cdot Al_2B(OH)Si_4O_{15}$ containing 9.5% boron), ore concentrate (15-17% boron), or boric oxide irritated the lungs and inhibited phagocytic activity in industrial workers.[92]

An daily ingestion of 3/4 of boric tartrate over a period of 20 years in one case resulted in chronic boric acid poisoning. The symptoms included cachexia, dermatitis, alopecia, hypoplastic anemia and gastric ulcer. All symptoms disappeared when the drug was withdrawn, but reappeared when therapy was resumed because of epilepsy.[130] No medical evidence of chronic effects of boron trifluoride has been found among workers exposed to small amounts for periods up to seven years. However, some workers in boron trifluoride, [illegible] complained of irritation of the eyes, nose and throat, [illegible] observed.[111]

B. Animals

1. Acute Toxicity

$LD_{50}$ doses of boric acid and borax were determined in rats as shown below:

| Sex & Strain | Boric Acid | Borax |
|---|---|---|
| Albino Sprague-Dawley | 5.14 | 2.66 |
| Wistar | 3.45 | 2.00 |
| Albino Sprague-Dawley | 4.08 | 2.56 |
| Wistar | 5.98 | 3.45 |

$LD_{50}$ levels could not be determined [illegible] because [illegible] how they were dispersed. The animals [illegible]

Acute effects of sodium perborate [illegible] were studied by intravenous and intraperitoneal [illegible] Acute toxicity was high with intraperitoneal [illegible]

reduced toxic effects of pentaborate more when intraperitoneally injected than intravenously injected.(132)

Methylene blue added to a five per cent dextrose infusion 20 minutes after administration of 40 mg/kg decaborane to rabbits followed by infusion of dilute methylene blue for 47 hours prolonged the life of the animals to over 24 or 48 hours. All untreated rabbits died within 24 hours.(133)

In monkeys, intraperitoneal injections of decaborane (6 mg per kg) resulted in death within three days. Daily injections of 1 mg per kg gave rise to an altered electroencephalogram characterized by a high frequency pattern of discharge and high voltage bursts in the hypothalamus.(134)

The $LC_{50}$ levels for inhalation exposures to pentaborane for mice and dogs were determined to be as follows:

| Time of exposure (min) | $LC_{50}$ ($mg/m^3$) | |
|---|---|---|
| | Mice | Dogs |
| 0.5 | 1,018 | -- |
| 2 | 142 | 734 |
| 5 | 136 | 324 |
| 15 | 50 | 92 |

The 2-minute $LC_{50}$ for [illegible] was 620 $mg/m^3$. Dogs and monkeys showed severe signs of intoxication after exposure to one half the $LC_{50}$ values, but not after one fourth or one eighth the $LC_{50}$ values. No notable changes in blood cell components, BUN retention time due to dyes or electrocardiographic lesions were observed. The conditioned avoidance response was altered after 1/2 $LC_{50}$ exposures.(135)

2. Chronic Toxicity

Effect levels in rats and dogs [illegible] decomposition to boron, and growth suppression and decreased food intake in both species. The "no effect" levels are shown below:

"No effect" Levels of Boron and Boron Compounds

| Species | Boron | Boron Oxide |
|---|---|---|
| Rat | 4600 | [illegible] |
| Dog | 1540 | 3000 |

ppm boron equivalent for both chemicals, but normal fertility, litter size, weight, and appearance occurred at the ppm boron equivalent.[136] In mice boric acid produced testicular atrophy with degeneration of the seminal cells.[137]

Dogs given drinking water containing two to three mg boron per liter had decreased gastric juice secretion and decreased free and total acidity. Enterokinase activity was inhibited in intestinal juice and feces.[51] Rats are relatively resistant to boric acid poisoning; they can survive daily doses up to 4 g/kg for 10 days or more. The males are more sensitive than the females. A 25% weight loss precedes death. Rats given boric acid in their drinking water died within two to six weeks, not only from the poisoning itself, but rabbits given boric acid by gavage lost more weight than dogs with up to 8% weight loss. Male rats exposed to 1% boric acid in their drinking water had testicular atrophy and lesions.[137]

In rats experimentally poisoned with boric acid, potassium hydrogen tartrate or tolbutamide (1-butyl-3-sulfanilyl-urea), urinary elimination was relatively rapid after single or repeated small doses, but was much slower with an increase in repeated doses than with other boron compounds. Placental passage led to a considerable diminution of vitality in young pregnant animals. Excretion through the milk was fairly rapid, lower concentrations occurred in some organs of chronically poisoned rats.[137]

Administration of boric acid to young rats for 30 days altered the shape of teeth.[138]

Daily intraperitoneal administration of 0.5 g boric acid per kg to rabbits for four months gave rise to a slight increase in the (120-150 mg per $m^3$) by rabbits, but there was a slight weight gain, increased nitrogen compounds in the urine and changes of the liver. Considerable changes in the respiratory tract, chronic tracheitis and bronchitis, with atrophy of the epithelium of the entire length of the tract.[52]

Marked inhibition of glycolytic enzymes and an increase in methemoglobin was observed in erythrocytes of guinea pigs with borate toxicity.(138) Groups of rats given boric acid and thiourea via a stomach catheter exhibited more pronounced thyroid enlargement and slowing of the heart than the control group of rats receiving thiourea alone. The largest decrease in rates of radioactive iodine uptake and clearance was also observed in the former group.(139)

Rats were exposed to aerosols of boron oxide for as long as 24 weeks. The highest concentration used was 470 mg per $m^3$ for 23 weeks. The mass median diameter of the particles was 1.9 to 2.5 microns. No deaths or other signs of intoxication were observed in rats exposed to aerosols of boron oxide at a concentration of 470 mg per $m^3$ for 10 weeks. Dogs exposed to 57 mg per $m^3$ exhibited increased urine volume, urine acidity and creatinine clearance.(140) Chronic intoxication with boric acid (0.20-0.80 g per kg) affected spermatogenesis in rats, depending upon the reproductive state of the testis. During the prepuberal period, boric acid had little effect on the testis, but during puberal crisis, boric acid exerts its strongest effects. Mitotic activity in the testis is greatly lowered, sometimes resulting in complete destruction of the spermatogenic line. There is only partial sensitivity to boric acid during the adult period.(141) Rats poisoned with sodium borohydride apparently die due to gaseous embolism subsequent to the discharge of hydrogen.(142) Bradycardia, elongation of the P-Q interval by 20%, and elongation of the electric systole by 10% were some of the cardiac rhythm changes observed in rabbits given 30 and 45 mg/kg doses of sodium borohydride by stomach tube.(143)

Decaborane (B10H14) applications to the skin of rats gave rise to hyperexcitation, aggressive behavior and central depression. Slight changes in the nerve cells were demonstrated.(144) The intraperitoneal injection of decaborane (20 mg per kg) to rats produced a strong increase in the levels of boron in the urine within a few hours after injection. This is apparently an effect on nitrogen metabolism and not a result of kidney injury.(145) Extensive changes in tissue amino acid levels followed boron administration in rats.(146)

caborane produced limitations of sympathetic activity evidenced by miosis, relaxation of the nictitating membrane, bradycardia, dilation of superficial vessels, and sedation with easy arousal. Anesthetized dogs showed an initial rise in blood pressure, followed by hypotension, bradycardia and decreased response to tyramine. Pentaborane is comparatively more active in producing excitement and convulsions.(136) Lethal injections of decaboranes in dogs produced a progressive decrease in heart force to terminal levels, but numerous intervening sustained intervals of hypertension were observed. Progressive EKG changes included decrease in P wave height, slow A-V nodal rhythms, occasional ectopic beats, and long periods of asystole.(145)

Intravenous perfusion of rabbits with various organoboron compounds revealed that the toxic effects of the di(pinacol)ester(tetraborate) of pentaerythritol were clearly distinguishable from the others. The symptoms produced by this drug included augmentation of blood pressure with tachycardia and apnea, interrupted by a sudden drop in blood pressure and bradycardia.(61) In rats and mice the toxicity of this compound was found to be relatively low. The sublethal dose (largest dose that can be given without causing mortality, however long the period of observation was) was over 1 g/kg intraperitoneally and 2 to 3.5 g/kg orally. Rats seemed to be more sensitive than mice. Sublethal doses did not produce any signs of toxicity, but larger doses produced prolonged coma up to 48 hours. The latent period for definite onset of action is two to four days. The recovery of survivors is rapid, with no apparent sequelae.(146)

c. Teratogenicity

Oral administration of 1.0 mg/g body weight to mice on the first day of pregnancy prevented 91.8% of the embryos cultured from reaching the blastocyst stage. Only 8.7% of the normal embryos failed to reach the blastocyst stage. Oral doses of 0.5 or 1.0 mg/g had similar but less significant effects. Addition of .1 and .01 mg/ml boric acid to embryo cultures from untreated mothers inhibited embryonic development to the blastocyst stage by 100% and 91% respectively.(147)

4. Allergic Reactions and Sensitization

No sensitization to boric acid or borax was found. In 99 patients treated for mycosis of the feet with Exoryco[C] gel containing 0.05% phenylmercuric borate, five cases of moderate irritation developed in patients who earlier had exhibited fatal reaction.[69] Applications of Zyma[C], containing 0.06% phenylmercuric borate, under an occlusive bandage produced irritation, but on bare skin, little or no response was observed.[70] Reaction to these gels is apparently due to mercury sensitivity.

Fetal lesions and cytotoxic effects in rat[150] and mouse[151] have been produced by thermal neutron boron-10 reactions with the skin following irradiation.

5. Behavioral Effects

Decaborane or its ions is known to have severe disruptive effects upon behavior.[124] Intraperitoneal injections of one mg per kg per day of decaborane to monkeys with implanted brain electrodes produced changes in the electroencephalogram consisting of high frequency patterns of activity, and high voltage bursts in the hypothalamus. Accompanying behavior included depression, somnolence, generalized twitching and short motor seizures.[134]

Boron-deficiency in plants apparently renders them unattractive to bees. Borax application restores the attraction. Boron apparently promotes nectar secretion.[152]

6. Carcinogenicity

No evidence has been produced for the role of boron as a possible carcinogen. Many studies on the high and selective uptake of boron by tumors have been done for possible use in neutron-capture cancer therapy.[153]

C. Nonmammalian Vertebrates

Boric acid treatment produces malformations in chicken and amphibian embryos. After injection of a twenty- to four-hour-old chicken yolk sac with 0.01 ml of sterile 5% boric acid solution, initial effects appeared in the young embryos. The neural tube, notochord, tail-gut and tail blastema were absent. Pyknosis of the indifferent cell mass of the tail blastema appeared in 20-25% of the boric-acid-treated embryos. Blood vasculature was not affected in these

rumpless chick embryos.(154) Boric acid also produced malformations in limb development in chicken embryos. The results were most clearly seen in the tarsometatarsus, which was bent backwards and severly shortened. Abnormal bends in the tibiotarsus were also seen. By day 11, the effect of boric acid may be the on chondrilling capacity, which affects the cartilage cells and the cartilage matrix, thus weakening the supporting body effect. Boric acid may further interfere with the process of extension of the collagen fibers, especially those of the sinews.(69)

Boric acid apparently exerts its teratogenic effects by complexation of polyhydroxy compounds, interfering with metabolism at the cellular level. Riboflavin content of livers of unincubated, normal chicken embryos was sharply reduced. Addition of riboflavin or polyhydroxy compounds such as ribose, sorbitol, etc., to the boric acid treatment decreased teratogenic effects. Plumage color of the mother has a definite effect on progeny response to boric acid. A lower incidence of boric acid-induced abnormalities was observed in the spring.(155)

When embryos of Bufo vulgaris were treated with 0.5% boric acid for 24 hours from the two cell stage to the tail bud stage, the malformations observed included edema, microcephalia with rudimentary stomodaeum or sucker, approaching of the olfactory pits, short tail and a reduction or lack of external gills. The epiphysis became bifurcated into a pair of vesicles of less vacuolized cells lying side by side. The forebrain showed a tendency to form a single tube with a narrow ventricle. Monorhiny, synrhiny, anophthalmia, cyclopia, and synophthalmia accompanied the suppression of forebrain development. The bifurcation of the epiphysis and the inhibition of sense organ development, together with the poorly developed forebrain, seem to be a result of the direct action of boric acid on the ectoderm.(156)

Vitamin C has been shown to decrease the phenylurea-urilorate intoxication of Rana temporaria tadpoles.(70)

D. Invertebrates

Boric acid has been demonstrated to be an effective stomach poison for several species of insects. The effect of mixtures of boric acid and sugar on the mortality of the German cockroach can be summarized as follows:(157)

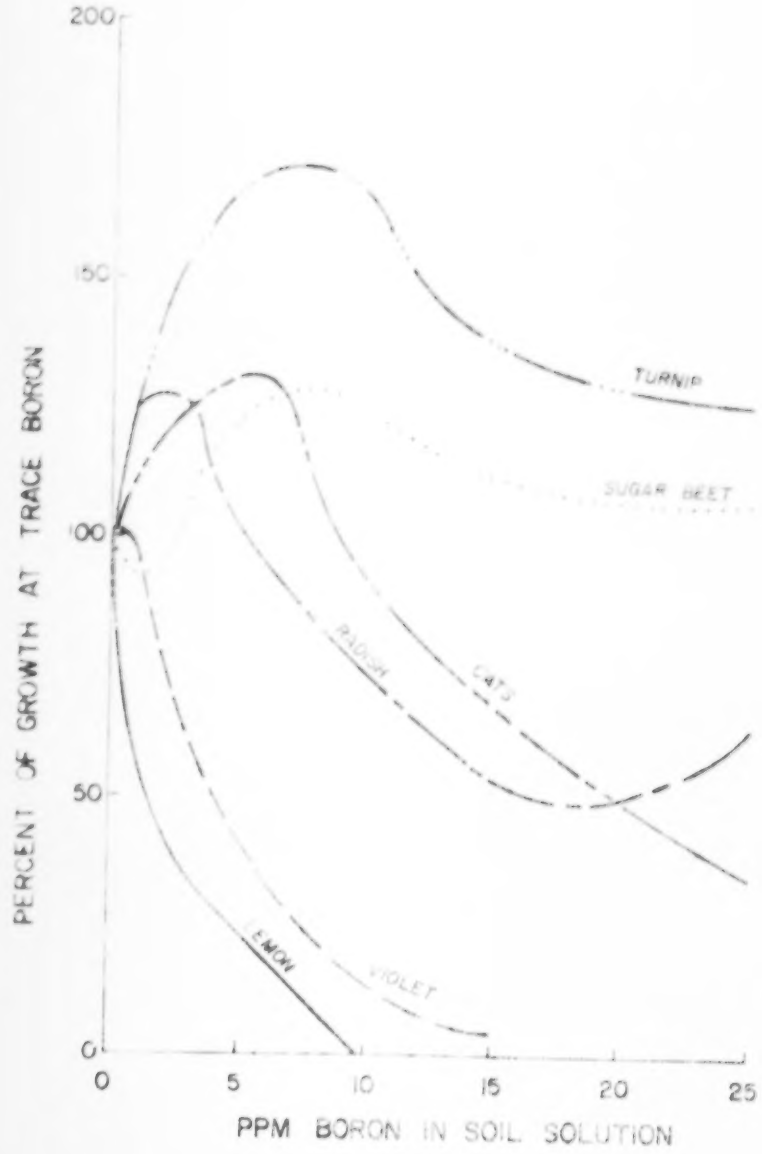


Figure 9

Effect of Boron concentration on plant growth

...with boron salts.[162] Treatment of wool with boric acid effectively controlled black carpet beetle larvae.[163]

...baited with cottonseed hydrolysate containing borax reduced infestation of navel oranges by fruit flies (Anastrepha ludens) by 68%, and in papayas, by 98%.[106]

The toxicity of organoboron compounds makes them useful as insecticides. Isobornyl thiocyanoacetate (IBTA) had an $LD_{50}$ of 27.3 micrograms per insect against domestic housefly. Aerosol bombs containing IBTA had a $KT_{50}$ (knock-down time) of six minutes. The effectiveness of IBTA was greatly decreased in concentrations below one per cent.[164] ...borony acetate from the volatile oils of anethum was the most toxic of the components of the oil to the larvae of Tribolium castaneum.[165]

Boric acid and other boron compounds have been demonstrated to be effective chemosterilants of the housefly, Musca domestica,[166, 167] and the cotton boll weevil.[105]

## E. Plants

Although boron is a nutritional requirement for most plants, too much boron is toxic. The dual effects of boron are illustrated in Figure 9,[168, 35] The amount of boron in saturation-extract concentrations of the soil is plotted against the plant weight expressed as a percentage of the average weight of the plant grown in soil containing trace boron.

Plants are classified as sensitive, semitolerant or tolerant to boron in soil extracts in two ways. Table 10 lists crop species in groupings based on the levels of boron in micrograms per ml of soil extract which produce toxic effects.[168] The most sensitive plants are listed at the top of each column. Plants are also classified into three categories based on a relative tolerance index. The index is 100 times the ratio of the average weight of plants grown in 5, 10 and 15 ppm boron to the largest weight of plants grown in either trace or 1 ppm boron[35] Table 11 summarizes this data.

The toxic symptoms of boron include stunted growth, deformed leaves, browning and yellowing, chlorosis and necrosis. Pollen germination and

[illegible]

[illegible]

| [illegible] | [illegible] | [illegible] |
|---|---|---|
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| Fig | [illegible] | [illegible] |
| Grape | [illegible] | [illegible] |
| Apple | [illegible] | [illegible] |
| Pear | [illegible] | [illegible] |
| Plum | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] |

*Listed in each category according to susceptibility to boron injury(viz., citrus is more sensitive than walnut, lima bean more than potato, etc.).

Table II.

Plant Growth as Affected by Boron (35)

| PLANT | Boron Conc. For Best Growth (ppm) | Lowest Conc. For Injury (ppm) | Relative Tolerance Index | Boron Deficiency Symptoms With Trace Boron* |
|---|---|---|---|---|
| **SENSITIVE PLANTS** | | | | |
| [illegible] | Trace | 1 | - | |
| [illegible] | Trace | 1 | - | S |
| [illegible] | 1 | 1 | - | None |
| [illegible] | 1 | 5 | - | S |
| [illegible] | 1 | 5 | - | S |
| [illegible] | 1 | 1 | - | Z |
| [illegible] | 1 | 1 | - | S |
| [illegible] | 1 | 5 | - | S |
| [illegible] | 1 | 1 | - | None |
| [illegible] | 1 | 1 | - | N |
| [illegible] | 1 | 5 | 9 | S |
| [illegible] | Trace | 5 | 20 | None |
| [illegible] | Trace | 5 | 24 | None |
| Cherry (Virgin Hibernia (Prunus [illegible] Sarg.) | 1 | 1 | - | None |
| Jerusalem artichoke (Helianthus tuberosus L.) | Trace | 5 | 30 | D |
| Larkspur (Delphinium sp.) | 1 | 1 | 34 | None |
| Zinnia (Zinnia elegans Jacq.) | 1 | 5 | 43 | S |
| | Trace | 1 | 45 | None |
| **SEMI-TOLERANT PLANTS** | | | | |
| Barley (Hordeum vulgare L.) | Trace | 5 | 51 | D |
| Pea (Pisum sativum L.) | 1 | 5 | 55 | None |
| Sweet Potato (Ipomoea batatas (Lam.) | Trace | 1 | 57 | S |
| Onion (Allium cepa L.) | Trace | 5 | 63 | S |
| Carrot (Daucus carota L.) | Trace | 1 | 68 | None |
| Red Pepper (Capsicum frutescens L.) | Trace | 10 | 70 | None |
| Kentucky Bluegrass (Poa pratensis L.) | 1 | 5 | 71 | None |
| Corn (Zea mays L.) | 1 | 1 | 86 | None |
| Potato (Solanum tuberosum L.) | 1 | 5 | 53 | None |
| Cabbage (Brassica oleracea var. capitata L.) | 1 | 1 | 78 | S |
| Milo (Sorghum vulgare Pers.) | Trace | 10 | 76 | None |
| Calendula (Calendula officinalis L.) | Trace | 5 | 80 | N |

Table II (Cont'd)

Plant Growth as Affected by Boron

| Plant | Boron Conc. for Best Growth (ppm) | Lowest Conc. for Injury (ppm) | Relative Tolerance Index | Boron Deficiency Symptoms with Trace Boron* |
|---|---|---|---|---|
| | | LOW-TOLERANT PLANTS (Cont'd) | | |
| Radish (Raphanus sativus L.) | 3 | 10 | 68 | S |
| Oats (Avena sativa L.) | 3 | 5 | 96 | None |
| Celery (Apium graveolens L.) | 15 | 25 | 69 | S |
| Mustard (Brassica | 3 | 10 | 94 | None |
| Parsley (Carum petroselinum | 3 | 10 | 85 | Crow |
| Alfalfa (Medicago | 10 | 15 | 106 | None |
| Lettuce (Lactuca sativa L.) | 3 | 1 | 96 | None |
| Kale (Brassica oleracea | 3 | 10 | 96 | None |
| Onion (Allium cepa L.) | 3 | 5 | 91 | None |
| Potato (Solanum tuberosum | 10 | 5 | 96 | None |
| California Privet | | | | |
| (Hesperocyparis californica (Carr.) | 3 | 5 | 99 | None |
| | | MEDIUM PLANTS | | |
| Turnip (Brassica rapa L.) | 3 | 25 | 115 | None |
| Common beet (Beta vulgaris L.) | 3 | 15 | 112 | S(?) |
| Leaf beet | | | | |
| (Beta vulgaris var. cicla L.) | 3 | 25 | 110 | S |
| Sugarbeet (Cucumis melo L.) | 5 | 5 | 107 | S |
| Sweet clover | | | | |
| (Melilotus indica(L.)All.) | 5 | 10 | 110 | None |
| Sweet pea (Lathyrus odoratus | 10 | 5 | 113 | S |
| Sugar beet | | | | |
| (Beta vulgaris var. saccharifera | | 15 | 121 | None |
| Garlic (Allium sativum L.) | 10 | None | 121 | S |
| Cotton (Gossypium hirsutum L.) | 10 | 25 | 130 | S |
| Artichoke (Cynara scolymus L.) | 5 | 5 | 123 | S |
| Asparagus | | | | |
| (Asparagus officinalis L.) | 51 | 25 | 217 | S |

*S: presence of leaf or other morphological abnormalities.
W: time of flowering or ripening substantially affected.
(?): trace-boron plants more severely attacked by mildew.
W: severe wilting.

...as petiole and growth may be inhibited. Symptoms of boron toxicity in various plant species are summarized in Table 12.

...necrotic lesions on petioles increased 657.7 ppm boron, while green ...increased 55.7 ppm.[170] In these leaves, 15 analysis of old leaf ...showed a boron content of 750 ppm dry weight basis, boron is the ...least mobile of nutrients.[170] In the tissue of a newly matured leaf of ...(above 200 ppm boron on dry weight basis), the boron ...injury will probably be severe enough at the time of harvest to make the ...unmarketable.[170]

...In leaf tissue culture, the reaction with cupferron ...boron from the tissue media. The practice of moving mature the ...concentration in the leaf tips.[171] The boron concentration of ...tissue may be 100 times higher than that in the petioles, and ...boron toxicity symptoms are reflected in this distribution.[171]

The addition of zinc to media containing high concentrations of boron reduces the degree of injury by boron.[172, 173, 174] 2-Chloroethanol apparently increases the boron resistance of wheat seedlings subject to boron toxicity.[175]

...Phenylboric acid (PBA) produces toxic effects at lower levels than boric ...acid. Addition of PBA (40 mg/l PBA to tomato, Lycopersicon esculentum, produced ...abnormalities of cell walls (PBA can be reversed with 100-500 mg/l boric acid.[176]

...Boron (5 ppm) in culture media caused pistils, stipistilly, and pistillody in ...plants resulted from a simple PBA treatment.[176] Lanceolate leaf ...was induced in Solanum lycopersicum by PBA.[176] The pollen of ...Datura metel seedlings was altered by a $2 \times 10^{-3}$ M solution of PBA.[177] ...stimulates the lanceolate ...to the tomato. In addition to a change in leaf form, increases in the activities of cytochrome, laccase, peroxidase, and catalase occur. It is suggested that the altered effects of the lanceolate gene, as well as PBA, produce increased oxidative enzyme activity, which results in an alteration in leaf form.[178]

Diarylboronic acids were toxic to wheat roots at $10^{-5}$ M. ...anisoleboronic acid hampered pollen germination and pollen tube growth.[179]

| Species | Soil level | Effect | Reference |
|---|---|---|---|
| cucumber | 5 ppm | 50% decrease in dry wt | (87) |
| squash | 10 ppm | 50% decrease in dry wt | (87) |
| muskmelon | 10 ppm | 50% decrease in dry wt | (87) |
| corn | 20 ppm | 50% decrease in dry wt | (87) |
| carnation (Dianthus caryophyllus) | 180 to 270 ppm | Decreased N and P leaf conc | (34) |
| Matthiola incana | 2.5 ppm | "Unmarketable crops" | (87) |
| peach | | Blockage of xylem of upper trunk and petioles with gum; wilting, leaf scorch | (21) |
| citrus | | Chlorotic leaves of fig and lemon; defoliation of lemon; absence of fig and walnut fruit production in other hosts | (210) |
| Chrysanthemum morifolium | | Stunted and distorted petioles; necrosis | (216) |
| groundnut | 10 ppm | Severe inhibition of leaves, shoots | (221) |
| horsebean | | Decrease in stem and epicotyl growth; interveinal chlorosis of young leaves; leaf curl and tuber necrosis | (213) |
| peach | | Delayed and poor blossoming; malformed fruits | (214) |
| sugar beet | | Radio-tagged uptake; decreased yield; increased N content | (189-74) |
| sunflower | | Morphological changes | (162) |
| Pinus radiata (pine) | | Increased uptake and concentration of Ca, P, Cu, Mg, Zn, Mn | (219) |

| Species | Boron levels | Symptoms | Reference |
|---|---|---|---|
| Setaria sphacelata | 50 ppm | Inhibition of pollen germination and pollen tube growth | (174) |
| tall wheat (Agropyron elongatum) | 33-38 ppm | 50% decrease in growth | (205) |
| maize | [illegible] | Reduced germination and pollen tube growth | (206) |
| citrus fruits | | Leaf chlorosis, reduced yield, poor fruit quality, smaller leaves | (207) |
| Citrus sinesis<br>Citrus reticulata | 0.4 [illegible] | tree collapse | (208) |
| berseem | [illegible] | water absorption affected | (192) |
| oats | 4.8 ppm | | (209) |
| cabbage | 11 ppm | | (209) |
| Kale | 100 lb/[illegible] | | (210) |
| red bean | 500-10 acres | reduced yield | (211) |

XI. [illegible]

A. Toxicity levels

LD50 [illegible] (42)

| Material | mg/kg of body weight |
|---|---|
| borax | 4050 |
| [illegible] | [illegible] |

Irritant to [illegible]

[illegible]

| Crop Species | [illegible] |
|---|---|
| Sensitive | [illegible] |
| Semi-tolerant | [illegible] |
| Tolerant | [illegible] |

Sensitive plants: [illegible], grape, [illegible], peach, persimmon, fig, strawberry, lupine, [illegible], [illegible], cherry, [illegible], avocado, artichoke, larkspur, zinnia.

The presence of boron in [illegible] concentration in [illegible] water is a potential [illegible] parts of western United States. [illegible] preplant [illegible] [illegible] [illegible]

Boron trifluoride is a nonflammable gas, requiring a green label. It is restricted to 140 kg in one outside container by rail express. IATA regulations permit the transport of up to 140 kg in cargo planes only.

Decaborane is classified as a flammable solid requiring a yellow label. Rail transport is limited to 12 kg in one outside container. IATA regulations permit cargo planes only to carry up to 12 kg of decaborane.

Pentaborane is a flammable liquid, requiring a red label. It is not accepted for rail express. IATA regulations prohibit its transport in both passenger and cargo planes.

C. Foreign Regulations

In the U.S.S.R the recommended maximum permissible concentration of calcium borate dust in the air of working locations is 4-6 $mg/m^3$ of air.(224)

XII. STANDARDS

Boron oxide - TLV - 10 $mg/m^3$. (225)

This value was recommended in view of the very low toxicity of test animals to boron oxide aerosols.

Boron trifluoride - TLV - 1 ppm* (approximately 3 $mg/m^3$). (225)

Boron tribromide - TLV - 1 ppm* (approximately 10 $mg/m^3$). (225)

*parts per million by volume

## XIII. SUMMARY AND CONCLUSIONS

### A. Summary

Boron is a ubiquitous element, found in 10 to 30 ppms in soils, about 0.1 ppm in surface waters, and 4.5 ppm in sea water. In spite of this, the domestic sources of boron raw materials are concentrated in the desert areas of California, and consequently the processing plants for these raw materials and those for production of bulk boron chemicals are located within a small region. The major raw material in this case is borax, which is the keystone of the boron industry. A consequence of this situation is that contamination of the environment from natural sources of boron materials is found within a relatively limited area.

Boron enters the environment at a rate of approximately 32,000 metric tons per year for the United States. Most of this ends up in the waters. About one-half of the total amount enters the water directly from laundry products and sewage.

Boron compounds are absorbed by the intestine, mucous membranes and skin. Excretion is mainly via the urine, but complete excretion is slow and boron may accumulate. Inorganic borates are quite toxic, apparently complexing hydroxy compounds and interfering with protein synthesis. Organoborate compounds exert physiological effects on the peripheral and central nervous system, acting as spasmolytics, sedatives and convulsants, depending upon the structure. Boranes produce toxic effects by creating embolisms of hydrogen gas as they react with tissue.

No boron carcinogenicity has been reported. Erythema and swelling may develop in individuals sensitive to boron. Boric acid is a potent teratogen when applied directly to the embryo. Boron compounds are selectively accumulated by some types of tumors and boron-10 compounds are used as neutron capture targets for tumor localization and treatment.

Boron is a growth requirement for plants and not for animals, but too much boron is phytotoxic. Plant species vary greatly in their sensitivity to boron toxicity. Boron compounds have been widely used as fertilizers, in-

secticides, fungicides, and bacteriocides.

The long range effects of boron compounds on fish and birds and other marine organisms have not been investigated.

Medical and household use of boric acid solutions as antiseptics has led to numerous accidental poisonings through ingestion or absorption through the skin, particularly in infants. Boric acid and borax are used as insect control compounds in wood preservation. Boric acid is also used to eradicate cockroaches.

B. Conclusions

The following conclusions are based on the material presented in this report on environmental effects of boron and its compounds:

1. Environmental contamination of the air with boron compounds does not appear to pose an environmental problem. Hazardous atmospheric conditions stemming from high concentrations of boron or its compounds is entirely localized.

2. Future build-up of boron in ground waters could cause detrimental effects to aquatic and other species of plants and animals. This is presently the case for areas where natural boron deposits are found. Plant toxicity effects could become generalized if boron-containing cleansing agents become more widely used in this country.

3. The acute toxicity of humans to boric acid has led to an inordinate number of poisonings which could probably have been prevented by minimal use of warning labels or substitution.

C. Recommendations

The following recommendations are based on the conclusions presented in Section XIII C above:

(1) Boron increases in U.S. waters should be closely studied with regard to effects on aquatic species should the use in this country of boron-containing cleansing agents increase significantly. Any detrimental effects should be noted first in Europe, where such usage of boron compounds is already intensive.

(2) Use of boric acid (and, perhaps, other boron-containing compounds) as externally applied antiseptics (or similar uses) should be discouraged because of its toxicity. Further study should be made to ascertain proper regulation in this case.

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